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Robert S. Kerr Environmental Research Lab.
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OZONE FOR INDUSTRIAL WATER AND WASTEWATER TREATMENT

An Annotated Bibliography

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Grant No. R-803357

to

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16. ABSTRACT

The project explored the technology of ozonation applicable to industrial water and wastewater treatment. The final report documents existing equipment, extent of application and practical usage, contract systems, monitoring and detection devices, general and specific economics, and most recent acceptable procedures.

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation'a land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized. EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

Increasing concern over the presence of toxic or nonbiodegradable components in treated effluents has dictated that research be performed to establish technologies for removal or conversion of those compounds to eliminate them from industrial wastewaters prior to discharge. Application of innovative technology, such as ozonation, to control undesirable contaminants in wastewater streams is of paramount interest as a potential treatment methodology to protect the environment.

William C. Galegar

W. C. Galegar
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ABSTRACT

This research project and technology transfer effort was initiated in response to growing national concern about the discharge of industrial chemicals and by-products from industrial processing plants into the environment. The technology of oxidation of these chemicals by means of ozone, a very powerful oxidant, offers promise for being able to eliminate some of these chemicals from industrial wastewaters prior to discharge. Therefore this program was initiated to survey the published ozone literature and assess how ozone has been used in the past to cope with specific industrial water and wastewater problems.

In the Literature Survey, which is a separate EPA report, there is included a section on the fundamental principles of ozone technology, which describes the generation of ozone on commercial scale, the various methods of contacting ozone with aqueous solutions and methods of analysis for ozone from the point of view of process controls.

Industries are grouped into 20 individual categories which are discussed separately as to the known uses of ozone in treating waters and wastewaters in each category. More than 500 published articles were reviewed. Some of these articles were abstracted, and these abstracts have been assembled in this companion report.

Abstracts are grouped according to their industrial categories, which are arranged alphabetically. A list of Literature Cited is given for each industrial category, and the cited articles are arranged alphabetically with respect to the last name of the senior author. Each article cited has been given a 2-letter category code and a number. For example, AQ-12 means the Aquaculture category, reference number 12.

An asterisk following the reference cited indicates that an abstract of that reference is included in this Annotated Bibliography.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AcH -- acetaldehyde
APHA -- American Public Health Association
bbl -- barrel
BOD -- biochemical oxygen demand
BOD-5 -- 5-day BOD
BPTCA -- best practicable control technology currently available
BuOH -- butyl alcohol (butanol)
cfm -- cubic feet per minute
cm -- centimeters
COD -- chemical oxygen demand
cP -- centipoise
cu ft -- cubic feet
DO -- dissolved oxygen
EDTA -- ethylenediaminetetra-acetic acid
Et -- ethyl
EtOAc -- ethyl acetate
EtOH -- ethyl alcohol (ethanol)
GAC -- granular activated carbon
gal -- gallon
g/hr -- grams per hour
gpm -- gallons per minute
gpd -- gallons per day
HCHO -- formaldehyde
HCOOH -- formic acid
hr -- hour
hp -- horsepower
Hz -- hertz
I -- imperial
ID -- inside diameter
Igpm -- imperial gallons/minute
in -- inch, inches
IR -- infrared
kg/sq cm -- kilograms/square cm
KHz -- kilohertz
kw -- kilowatt
kwh -- kilowatt-hour
M -- molar
Me -- methyl
MeOH -- methyl alcohol, methanol
mg/l -- milligrams per liter
min -- minute
MM -- million
MUST -- mobile unit, self transportable
nm -- nanometer
NMR -- nuclear magnetic resonance
NSSC -- neutral sulfite semi-chemical
OAV -- oxygen absorption value
OD -- outside diameter
PAC -- powdered activated carbon
ppb -- parts per billion
ppm -- parts per million
PSIG -- pounds per sq in guage
P.V. -- permanganate value
PVC -- polyvinyl chloride
RFI -- refractory index scale
RO -- reverse osmosis
RPM -- revolutions per minute
SCFH -- standard cu ft/hr
scfm -- standard cu ft/min
sec -- second
sq m/hr -- square meters per hour
SS -- suspended solids
std l/min -- standard liters/minute
TDS -- total dissolved solids
TLC -- thin layer chromatography
TOC -- total organic carbon
UF -- ultrafiltration
US -- ultrasonics
UV -- ultraviolet
v -- volt
wh/g -- watt hours/gram
yr -- year

SYMBOLS

[ ] -- concentration of
μ -- micron

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We also thank Dr. Walter J. Blogoslawski of the National Marine Fisheries Service for critically reviewing those sections of this report dealing with aquaculture and biofouling, Dr. L. Joseph Bollyky of Bollyky Associates for reviewing the sections dealing with cyanides and cyanates as well as electroplating, and Captain Barry W. Peterman of the Army Medical Bioengineering Research & Development Laboratories for reviewing the section on hospital wastewaters.

INTRODUCTION

Although ozone has been used to treat drinking water at the city of Nice since 1906, and today there are more than 1,000 water treatment plants in Europe alone employing ozone for many different water treatment purposes (Miller et al., 1978), industrial wastewater treatment with ozone is still, relatively speaking, in its infancy.

Current water pollution problems with industrial wastewater discharges have prompted renewed interest in the use of powerful oxidants, including ozone, for treating these wastewaters for recycle and reuse, or prior to discharge to the environment.

In addition, where halogenated oxidants such as chlorine and hypochlorite are currently used to treat municipal and industrial wastewaters, toxicities of these halogenated wastewaters to indigenous aquatic life also have prompted studies on alternative treatment techniques, including ozonation.

In recognition of the potentials for ozone to alleviate certain industrial wastewater pollution problems, the U.S. Environmental Protection Agency, Office of Research & Development, funded a grant (R-803357-01-3) to the International Ozone Institute to conduct a state-of-the-art review of the published literature dealing with the use of ozone. This report will summarize the results of that survey.

This survey is not an exhaustive review of the published literature, in that only the more readily available articles were obtained. In addition, much of the Russian, Japanese and German literature could not be translated due to limitations of time and funding. Nevertheless, some 430 published articles were reviewed and abstracted. Abstracts of the more pertinent articles have been compiled in this companion report.

LITERATURE CITED -- AQUACULTURE (AQ)

AQ-01 Anonymous, 1972, "Use of Ozone in Sea Water for Cleansing Shellfish", Effluent and Water Treatment Journal, 12:260-262.

AQ-02 Blogoslawski, W.J., 1977, "Ozone as a disinfectant in mariculture", in Proc. Third Meeting of the I.C.E.S. Working Group on Mariculture, Brest, France, May 10-13. Actes de Colloques de C.N.E.X.O. 4:371-381.

AQ-03 Benoit, R.G. & N.A. Matlin, 1966, "Control of Saprolegnia on Eggs of Rainbow Trout *(Salmo gairdneri)* with Ozone", Trans. Am. Fish Soc. 95(4):430-432.

AQ-04* Blogoslawski, W.J., C. Brown, E.W. Rhodes & M. Broadhurst, 1975, "Ozone Disinfection of a Seawater Supply System." in *Proc. First Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, Editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 674-687.

AQ-05 Blogoslawski, W.J., F.P. Thurberg & M.A. Dawson, 1973, "Ozone Inactivation of a *Gymnodinium breve* Toxin." Water Research 7:1701-1703.

AQ-06* Blogoslawski, W.J., F.P. Thurberg, M.A. Dawson & M.J. Beckage, 1975, "Field Studies on Ozone Inactivation of a *Gymnodinium breve* Toxin", Environmental Letters, 9(2):209-215.

AQ-07 Blogoslawski, W.J., L. Farrell, R. Garceau & P. Derrig, 1976, "Production of Oxidants in Ozonized Seawater", in *Proc. Sec. Intl. Symp. on Ozone Technol.*, R.G. Rice, P. Pichet & M.-A. Vincent, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 671-681.

AQ-08 Blogoslawski, W.J. & M.E. Stewart, 1977, "Marine Applications of Ozone Water Treatment", in *Forum on Ozone Disinfection*, E.G. Fochtman, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 266-276.

AQ-09 Blogoslawski, W.J. & M.E. Stewart, 1978, "Paralytic Shellfish Poison in *Spisula solidissima*: Anatomical Location and Ozone Detoxification", Marine Biology, *in press*.

AQ-10* Burkstaller, J. & R.E. Speece, 1970, "Survey of Treatment and Recycle of Used Fish Hatchery Water." New Mexico State Univ. Engr. Exptl. Sta., Technical Rept. #64, June.

AQ-11 Ciambrone, D.F., 1975, "Ozone Treated Sewage for Oyster Culture", in *Aquatic Applications of Ozone*, W.J. Blogoslawski & R.G. Rice, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 81-86.

AQ-12 Combs, T.J. & W.J. Blogoslawski, 1975, "Effects of Ozone on a Marine-Occurring Yeast, Sporobolomyces", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 43-49.

AQ-13 Crecelius, E.A., 1977, "The Production of Bromine and Bromate in Seawater by Ozonization", presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov. Intl. Ozone Assoc., Cleveland, Ohio.

AQ-14 Dawson, M.A., F. Thurberg, W.J. Blogoslawski, J. Sasner, Jr. & M. Ikawa, 1974, "Inactivation of Paralytic Shellfish Poison by Ozone Treatment", Proc. Food-Drugs from the Sea Conf., Marine Technology Soc., p. 152-157.

AQ-15* DeManche, J.M., P.L. Donaghay, W.P. Breese & L.F. Small, 1975, "Residual Toxicity of Ozonized Seawater to Oyster Larvae." Oregon State Univ., Sea Grant College Prog. Pub. #ORESU-T-75-003, November, 5 pp.

AQ-16 Edwards, H.B., 1974, "Closed Raceway System for Mariculture", 1974, Presented at World Mariculture Soc. Meeting.

AQ-17 Edwards, H.B., 1975, "A New Concept for Aquaculture Closed Raceway Systems", Presented at World Mariculture Society, Seattle, Washington, Jan. 30.

AQ-18 Eppley, R.W., E.H. Renger & P.M. Williams, 1976, "Chlorine Reactions With Seawater Constituents and the Inhibition of Photosynthesis of Natural Marine Phytoplankton", Estuarine & Coastal Marine Sci. 4:147-161.

AQ-19* Fauvel, Y., 1963, "Use of Ozone as a Sterilizing Agent in Seawater for the Depuration of Shellfish", Intl. Comm. for Scientific Exploration of the Mediterranean Ocean, Reports and Verbal Proceedings 17(3):701-706.

AQ-20 Fauvel, Y., 1964, "Nouvelles observations sur l'utilisation de l'ozone comme agent stérilisateur de l'eau de mer pour l'épuration des coquillages", Comm. Int. Explor. Sci. Mer Médit., Symp. Pollut. Mar. par Microorgan. Prod. Pétrol. 293-298.

AQ-21 Fauvel, Y., 1967, "l'Epuration des Coquillages", Rev. trav. Inst. Pêches marit., 31(1).

AQ-22 Fauvel, Y., 1977, "Utilisation de L'Ozone en Ostreiculture et dans les Industries Connexes", Presented at 3rd Intl. Symp. on Ozone Technol., Paris, France, May. Intl. Ozone Assoc., Cleveland, Ohio.

AQ-23 Frese, R., 1974, "Ozonisierung odor Biologische Filterung. Eine Vergleichende Studie mit Einbeziehung der Erfahrungen am Kieler Aquarium". Diplomarbeit Christian Albrecht. Univ. Kiel, 58 p.

AQ-24 Giese, A. & E. Christensen, 1965, "Effects of Ozone on Organisms", Physiol. Zool. 27(2):101-115.

AQ-25 Haraguchi, T., U. Simidu & K. Aiso, 1969, "Preserving Effect of Ozone to Fish", Bull. Japanese Soc. Sci. Fisheries, 35(9).

AQ-26 Helz, G.R., R.Y. Hsu & R.M. Block, 1978, "Bromoform Production by Oxidative Biocides in Marine Waters", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 68-76.

AQ-27 Honn, K. & W. Chavin, 1976, "Utility of Ozone Treatment in the Maintenance of Water Quality in a Closed Marine System", Marine Biol. 34:201-209.

AQ-28 Ingols, R.S., 1978, "Ozonation of Seawater", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 77-81.

AQ-29 Macalady, D.L., J.H. Carpenter & C.A. Moore, 1977. "Sunlight-Induced Bromate Formation in Chlorinated Seawater", Science 195:1335-1337.

AQ-30* MacLean, S.A., A.C. Longwell & W.J. Blogoslawski, 1973, "Effects of Ozone-treated Seawater on the Spawned, Fertilized, Meiotic and Cleaving Eggs of the Commercial American Oyster." Mutation Rsch. 21:283-285.

AQ-31 Murphy, W.K., 1975, "The Use of Ozone in Recycled Oceanarium Water", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 87-95.

AQ-32 Pichet, P. & C. Hurtubise, 1975, "Reactions of Ozone in Artificial Seawater", in Proc. Sec. Intl. Symp. on Ozone Technol., R.G. Rice, P. Pichet & M.-A. Vincent, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 665-681.

AQ-33 Rosenlund, B.D., 1975, "Disinfection of Hatchery Influent By Ozonation and the Effects of Ozonated Water on Rainbow Trout", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 59-69.

AQ-34* Salmon, J., A. Salmon, J. Le Gall & D. Loir, 1937, "A Depuration Station for Shellfish Using Ozonized Seawater." Ann. Hyg. 15:581-584.

AQ-35* Salmon, J., J. Le Gall & A. Salmon, 1937, "Preliminary Note on Several Experiments of Purifying Edible Marine Molluscs by Ozonized Seawater", Ann. Hyg. Publique, Industrielle et Sociale 15:44-50.

AQ-36 Sander, E. & H. Rosenthal, 1975, "Application of Ozone in Water Treatment For Home Aquaria, Public Aquaria and for Aquaculture Purposes", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 103-114.

AQ-37 Spotte, S.H., 1970, Fish and Invertebrate Culture: Water Management in Closed Systems, Wiley-Interscience Publishers, Inc., New York, N.Y., 145 p.

AQ-38 Stewart, M.E. & W.J. Blogoslawski, 1977, "Detoxification of Marine Poisons By Ozone Gas", Presented at 3rd Intl. Symp. on Ozone Technol., Paris, France, May. Intl. Ozone Assoc., Cleveland, Ohio.

AQ-39 Stopka, K., 1975, "European and Canadian Experiences with Ozone in Controlled Closed Circuit Fresh & Salt Water Systems", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 170-176.

AQ-40 Tchakhotine, S., 1937, "The Destructive Action of Ozone on Sperm", Compt. rend. de Soc. de Biologie 126:1154-1156.

AQ-41 Thompson, G.E., 1976, "Ozone Applications in Manitoba, Canada", in Proc. Sec. Intl. Symp. on Ozone Technology, R.G. Rice, P. Pichet & M.-A. Vincent, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 682-693.

AQ-42 Thurberg, F.P., 1975, "Inactivation of Red-Tide Toxins by Ozone Treatment", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 50-58.

AQ-43* Violle, H., 1929, "Sterilization of Seawater with Ozone: Application of this Method to the Purification of Contaminated Shellfish", Rev. Hyg. et de Med. Preventive 51:42-46.

AQ-04

Title: "Ozone Disinfection Of A Seawater Supply System"

Authors: W.J. Blogoslawski, C. Brown, E.W. Rhodes & M. Broadhurst

Source: Proc. First Intl. Symposium on Ozone for Water & Wastewater Treatment, R. G. Rice & M. E. Browning, Editors, Intl. Ozone Assoc., Cleveland, Ohio (1975), p. 674-687.

Describes a 13,000 gpd pilot scale seawater disinfection system at the Milford, Connecticut Laboratory of the National Marine Fisheries Service. It was designed to eliminate fouling associated with piping volumes of seawater and reduce the possibility of marine microorganisms pathogenic to fish, molluscs, and crustaceans. In addition, the process demonstrated the ability of aeration to reduce the toxicity of phytoplankton metabolites during midsummer bloom of Long Island Sound "red tides".

System Description: Raw seawater is gravity delivered to a magnetic drive centrifugal pump and lifted through a 1.7 cu ft vertical packed column containing 8 x 12 mesh coconut shell activated carbon (Calgon Corp., Type PCB). After prefiltration, the water is passed through 2 static mixing columns (Kenics Corp. Model 37-56-092) in vertical series with a total of 24 PVC mixing elements. Ozone gas in compressed air is introduced counter-currently at the base of the mixing column by a 6 g/hr capacity ozone generator (PCI Ozone Corp.) at a flow of 20 SCFH. (The concentration of ozone in the air feed gas is not given, therefore, ozone dosage and ozone utilization cannot be calculated with certainty.)

Ozonized seawater then is pumped up through 3 parallel column filters containing 10.2 cu ft of 6 x 16 mesh coconut shell activated carbon. Treated water is passed through 2 10-micron mesh nylon filter bags and stored in a 750 gal fiberglass-lined holding tank. Water production is controlled by float switches located in the storage tank. When the system is not treating water the carbon columns are automatically back-flushed with well water at 45 PSIG. The cumulative backwashing time amounts to 11 or 12 hrs/day. Dissolved ozone is determined from samples taken prior to carbon filtration by an amperometric ozone analyzer (Fisher & Porter, Model 17L-2000). No ozone is found in the effluent from the carbon columns. Water quality is monitored by total plate counts taken weekly. Samples of the raw and ozonized water are plated on marine agar and incubated for 5 days at 18°C.

Plate counts were taken over 1 yr of normal operation to monitor disinfection efficiency. Entering bacterial concentrations were 10^5 to 10^3/ml. Counts in the ozonized seawater were at least 2 to 3 log numbers less than in the raw water. At a dissolved ozone concentration of 0.5 to 0.56 mg/l, no microorganisms were observed on inoculated agar plates. This residual ozone concentration was obtained at a 7 gpm flow and 30 sec residence time in the ozone reactor (20°C). If the generator was producing at its maximum rate (6 g/hr), then the ozone dosage required to attain the residual of 0.5 to 0.56 mg/l was 3.77 mg/l. However, ozone utilization cannot be calculated, since the amount of ozone in contactor off-gases was not determined.

During the pilot study, marine fish, crustaceans and molluscs freshly captured from Long Island Sound were held in flow-through 250 gal tanks containing either raw or ozonized water. In groups without water treatment, fish developed whitish lesions near the fins or tail characteristic of the salt water aquaria disease "fin rot". Mortality ranged from 78 to 100% over a 90 day test period. No fin rot or necrotic lesions were noticed, and limited mortality occurred in fish held in ozone treated water.

Ozonized water prevented fertilized oyster eggs from developing into normal larvae. In a 68-hr test only 44.2% of the eggs developed normally in ozonized water. Toxicity cannot be caused by residual ozone due to its short half-life and because dissolved ozone is destroyed upon passage of the treated water through activated carbon. Therefore it is concluded that toxic activity is caused by some oxidation product (organic or inorganic).

The ozone contactors, associated piping and after-filters have remained free of fouling organisms. Non-ozonized seawater pipes become heavily fouled over a 3 day period. This indicates a potential for ozone to control biological fouling.

AQ-06

Title: "Ozone Inactivation Of A *Gymnodinium breve* Toxin"

Authors: W.J. Blogoslawski, F.P. Thurberg & M.A. Dawson

Source: Water Research 7:1701-1703 (1973).

Discusses the ability of ozone to inactivate toxic metabolites of the Florida red tide dinoflagellate, *Gymnodinium breve*.

Crude toxic material was obtained by ether extraction of *Gymnodinium breve* cultures. The toxic powder was suspended in mammalian saline and injected intraperitoneally (i.p.) into 19 to 21 g white mice. A similar preparation was suspended in seawater and injected i.p. into 6 to 10 g killifish. Mouse dosage was 6.0 mg toxin in 0.4 ml saline, and the fish dosage was 6.0 mg in 0.2 ml saline. After data were obtained on the toxicity of the sample, the material was ozonized.

Three ml samples (toxin suspended in appropriate saline) were placed in 2-dram glass vials and ozone bubbled through the solution via a 21-gauge hypodermic needle. A small magnetic bar was placed in each vial to allow continuous stirring during ozonization and all samples were treated 15 min. The ozone (1% by wt in compressed air) was generated by a Marine Water Purifier with a rated capacity of 2.0 g/hr (PCI Ozone Corp.). The gas flow rate was determined by a Gilmont flow meter (size 1).

The results of ozonization of toxin, as tested by mouse and fish injection are shown in Table 1.

The authors conclude that the study demonstrated the potential use of ozone water treatment as a method of detoxifying red tide water prior to use in aquarium systems, provided no ozone residual remains in the water. Residual ozone may be removed by filtration through activated carbon.

The authors do not state the ratio of ozone dosage to toxin removed, however this was calculated from the description of the experiment. An ozone gas concentration of 1% by wt is equivalent to about 12 mg ozone/l of gas. Bubbling 15 min at the rate of 0.11 liter/min corresponds to an applied dose of 19.8 mg of ozone. The 3 ml soln of toxin in saline for use on the mice contained 45 mg of toxin; that for use on killifish contained 90 mg of toxin.

From the table it can be seen that this amount of toxin was deactivated by the preceding dosage of ozone. Data are not given for the amount of ozone in the off-gases, so that the amount of ozone utilized cannot be determined.

TABLE 1. EFFECTS OF OZONATION OF *GYMNODINIUM BREVE* TOXIN ON MICE AND KILLIFISH

MICE (*Mus musculus*)			
ml O_3/min	No. of Animals	Death time(min)	No. Alive(48 hr)
110	10	-	10
65	10	146-178	8
40	5	96-166	2
20	5	18-40	0
0	10	7-10	0
KILLIFISH (*Fundulus heteroclitus*)			
ml O_3/min	No. of Animals	Death time(min)	No. Alive
110	25	240-360	23
0	25	15-30	0

AQ-10

Title: "Survey of Treatment and Recycle of Used Fish Hatchery Water"

Authors: J. Burkstaller and R.E. Speece

Source: New Mexico State University, Engineering Experiment Station, Technical Report No. 64, June 1970.

Reuse of fish hatchery water is becoming more attractive for the following reasons: (1) many water supplies are too cold and must be heated, and on a once-through basis all heat remaining is wasted; (2) many areas do not have sufficient water supplies to raise full capacities of fish during dry months, and (3) spatial limitations are also becoming increasingly prevalent. Problems encountered in recycling of hatchery water include:

(1) Smaller fish are much more susceptible to certain fish diseases and recycle can take disease-producing organisms from older fish and start an epidemic among the younger fish; (2) ammonia is extremely toxic to fish even in very small amounts, and therefore, it must be removed from the water before reuse; and (3) for growing cold water fish, recycle water may become unsuitable since it eventually warms to the temperature of the surroundings.

Various treatment methods tested to alleviate these problems include the use of UV light, chlorine, bromine, chlorine-bromine combinations, and the suggested use of ozone for disinfection. Use of these methods, however, would require additional treatment for residual removal. A typical installation involving U-tube aeration, biological filters for nitrification, and continuous monitoring of pH, DO and temperature is presented.

AQ-15

Title: "Residual Toxicity of Ozonized Seawater to Oyster Larvae"

Authors: J.M. DeManche, P.L. Donaghay, W.P. Breese & L.F. Small

Source: Oregon State Univ. Sea Grant Program, Publ. No. ORESU-T-75-0003, Oregon State Univ. School of Oceanography, Nov. 1975.

Ozonation Equipment: An Alron Industries Model WP-4 ozone generator was fed with dry oxygen to produce 0.5 to 0.75 g ozone/hr, which was dispersed through a medium porosity glass frit into seawater which had been filtered through an 0.8 μ pore size Millipore filter. No data are given from which ozone utilization can be calculated.

Procedure: Ozonized water was treated as follows:

1) aged at room temperature for up to 4 weeks (to allow ozone to decompose)
2) ambient air was bubbled 1 week through 1 liter of ozonized seawater
3) ozonized seawater was vacuum filtered through an 0.8 μ Millipore filter
4) 20 mg/l sodium EDTA solution was added to ozonized seawater (to remove any heavy metals that may have been decomplexed by ozonizing
5) vacuum filtered through a 0.5 to 4 cm thickness of activated carbon above the Millipore filter
6) gravity filtered through a column (2.5 cm diameter x 20 cm length) containing 100 cc of charcoal granules. Several types of charcoal were tested
7) autoclaved 5 min at 15 lbs/sq in (1.0 kg/sq cm)

Bioassays were conducted in replicate. 150 freshly fertilized oyster eggs (*Crassostrea gigas*) were placed in approximately 100 ml of treated seawater, and the degree of toxicity determined by counting the number which showed normal growth after 24 hrs. Control values above 80% indicated valid bioassays.

Results: Ozonized seawater causes a long term residual toxicity to oyster larvae. Allowing ozonized seawater to stand up to 4 weeks (so as to allow ozone decomposition back to oxygen) did not reduce this toxicity. Neither did bubbling air through ozonized seawaters. Treatment with EDTA removed heavy metals, but had no effect on the residual toxicity. The only effective treatment was filtration through activated carbon, but the effectiveness of various types of charcoal was highly variable. Darco granular coconut charcoal was found to have a toxicity of its own. Darco D-60 (20 to 40 mesh) satisfactorily removed toxicity caused by ozonation.

Ozonization appeared to be effective in enhancing the quality of seawater, when the toxicity was removed by activated carbon.

AQ-19

Title: "Use of Ozone as a Sterilizing Agent in Seawater for the Depuration of Shellfish"

Author: Y. Fauvel

Source: Intl. Commission for Scientific Exploration of the Mediteranean Ocean, Reports and Verbal Proceedings 17(3):701-706 (1963).

Ozone depuration of shellfish was proposed in 1929, but was not used industrially until the early 1960s.

Two lots of 200 kg of bacterially contaminated mussels were treated 24 hrs in each of 2 tanks (48 hrs total treatment). The concentration of mussels in seawater was 5 kg/sq m. Bacterial contamination of mussel flesh and intervalve liquid was determined. Initial flesh contamination of 45,000 to 60,000 coliforms/l was reduced in 24 hrs to 600 to 2,400 and to zero in 48 hrs of depuration.

Similarly, 10 kg of clams were depurated in 300 l of seawater at a concentration of 30 kg of clams/sq m. At the time the clams were placed in the tank, tissue pollution was 60,000 coliforms/l. The count had fallen to 18,000 after 24 hrs, to 3,000 after 48 hrs, and to zero after 72 hrs. In the intervalve liquid, the coliforms/l were 400 after 72 hrs. Depuration of clams is slower than that of mussels.

Another 20 kg of clams were fished from unhealthy zones near Sète (France) and held 48 hrs near sewer outfalls. They were then divided into 2 lots, each placed in a 300 l container and stored in chlorinated seawater and in ozonized seawater. At the start, tissue coliform counts were 120,000/l in both samples. Data obtained with time are listed in Table 2.

Thus depuration with ozonized seawater is preferred over chlorinated seawater, because depuration is attained faster. In addition, shellfish depurated in ozonized seawater retain their original taste, whereas those treated in chlorinated water appear soft and chewey. Finally, no detrimental health effects were observed in shellfish treated in ozonized seawater.

TABLE 2. DEPURATION OF CLAMS IN OZONIZED SEAWATER

	tissue coliform counts	
days exposure	chlorinated water	ozonized water
start	120,000 coliforms/l	120,000 coliforms/l
48 hrs	90,000 "	90,000 "
72 hrs	60,000 "	6,000 "
4 days	24,000 "	1,800 "
5 days	1,200 "	0 "
5 days	400* "	100* "
5 days	20 dead individuals	8 dead individuals

* intervalve liquid coliform counts

AQ-30

Title: "Effects of Ozone-Treated Seawater On The Spawned, Fertilized Meiotic and Cleaving Eggs Of The Commercial American Oyster"

Authors: S.A. MacLean, C. Longwell & W.J. Blogoslawski

Source: Mutation Research 21:283-285 (1973).

Discusses a number of adverse effects which appear to be caused by residual ozone and/or its decomposition products upon eggs of the commercial American oyster. Seawater was passed through 2 Dynel filters to remove particulate matter larger than 15 μ in diameter. A portion of the water was then ozonized at 30 SCFH in a 15 liter bucket for 3 min (2% ozone-air mixture). The ozone-treated water was allowed to stand in the open bucket for 2 hrs during which time the ozone residual level decreased to approximately 0.18 mg/l.

Eggs were held in treated and control water up to 2 hrs at which time the last cytological fixation was made. Results are summarized in Table 3.

Unfertilized eggs spawned by the same female in the control and in treated water showed no cytological diffs. Fertilization occurred less readily in the treated water, as evidenced by a decrease in polyspermy and an increase in parthenogenesis. This is also indicated by the larger number of eggs (more than double) retarded in their completion of meiosis, the increased incidence of abnormal polar bodies in eggs held in the ozonized water (more than triple the number of eggs), and the larger numbers of cleaving eggs with abnormal nuclei (more than double). These nuclei showed signs of metabolic difficulties or of degeneration, and were pycnotic, pale, diffuse, or even fragmented. The background incidence of abnormalities in the control sample is not atypical for this invertebrate.

TABLE 3. EFFECTS OF OZONIZED SEAWATER ON SPAWNED, FERTILIZED MEIOTIC AND CLEAVING OYSTER EGGS

Effect or Condition Scored	Total Number of Eggs Observed	% of Eggs Spawned, Fertilized & Held in Control Seawater	% of Eggs Spawned, Fertilized & Held in Ozone Treated Seawater	Ratio O_3/Control
Polyspermy	400	9.0	1.75	0.2
Parthenogenesis	200	9.0	18.0	2.0
Retarded meiosis & cleavage	200	12.5	28.0	2.2
Irregularity of polar bodies	400	5.0	16.0	3.2
Abnormal cleavage	200	19.5	41.5	2.1

The authors concluded that for ozonized seawater:

1. Additional work is necessary to clarify whether the effects are due to ozone or to the by-products of its oxidation of impurities in the seawater.

2. The cytological and cytogenetic effects of ozone appear to be radiomimetic. This may be due to the positive radical ($OH^\bullet$ and $HO_2^\bullet$) decomposition products of ozone which are considered to be the biologically active products of irradiation of protoplasm.

3. The presence of fragment nuclei indicate that there likely was some chromosome breakage. This is in agreement with other investigations of ozone damage to cells.

4. The increased parthenogenesis and decreased polyspermy may be attributable to the effect of ozone on the membranes of the oyster egg.

5. Such consequences of ozonization might be accepted knowledgeably along with the benefits. Practical post-ozonation steps, such as carbon adsorption, possibly could be developed to remove the offending substances.

A reservation stated by the authors is that "just how much residual ozone and the products of its decomposition were present in the seawater by the time the oyster eggs were spawned in it is uncertain."

AQ-34

Title: "A Depuration Station for Shellfish Using Ozonized Seawater"

Authors: J. Salmon, A. Salmon, J. LeGall and D. Loir

Source: Ann. Hyg. 15:581-584 (1937)

Pathogenic bacteria which can cause typhoid fever do not remain in the bodies of shellfish bathed in seawater. A prolonged residence time of shellfish in seawater allows progressive elimination of these bacteria. If the seawater in which the shellfish are bathed (depurated) is also ozonized, these pathogenic bacteria will be killed by the action of the ozone.

Tests are described of shellfish depuration at the cities of Hâvre and of Boulogne-sur-Mer using ozonized seawaters. Shellfish to be cleansed are placed in baskets in 2 or more superimposed beds. They are submerged and rinsed with ordinary seawater which cleanses them of impurities adhering to the outside of the shellfish. The baskets then are transported by conveyer belt to a first cleansing tank where they are kept 24 hrs in ozonized seawater. In this tank the molluscs clean entrained bacteria from their intestines. The bacteria are killed by the action of ozone.

After 24 hrs of cleansing, a rinse in ozonized seawater completes the first treatment. The baskets then are sent to a second sterilization tank where they are kept until ready for packaging and shipment to market. The following are the pertinent treatment parameters:

Av wt of shellfish (mussel)	7-10 g
No of mussels/l	100
Amount of ozonized water/mussel/hr	20 ml

Oysters and other shellfish have different filtration coefficients, thus these conditions should be modified.

The system at Hâvre cleanses 2,000 kg/day of shellfish; that at Boulogne-sur-Mer cleanses 6,000 kg/day.

An Otto ozone generator is used at each station, but dosages and contact times for the ozonation are not described.

AQ-35

Title: "Preliminary Note on Several Experiments of Purifying Edible Marine Molluscs by Ozonized Seawater"

Authors: J. Salmon, J. Le Gall and A. Salmon

Source: Ann. Hyg. Publique, Industrielle et Sociale 15:44-50 (1937)

Preliminary tests made at the zoological station of Wirmereux are described. An Otto plate type ozone generator, Model 102, generating 500 l/hr of ozonized air was employed, but the contacting and ozone contact times and doses are not described. Ozonation was intermittent, not continuous.

Oysters, mussels and other varied local shellfish were subjected to bacterial analyses, then were stored in ozonized seawaters for varying lengths of time, then analyzed again.

First pathogenic bacteria, then coliforms, then coli-bacillus disappear on exposure (depuration) of shellfish in ozonized water. The minimum time for depuration was not determined exactly, but is less than 4 days exposure. Mussels were depurated in 24 hrs maximum. Oysters and other shellfish stored 48 hrs in freshly ozonized seawater showed complete destruction of all pathogenic bacteria. Addition of ozonized seawater did not create any noxious substance for treated molluscs; no change in health of the molluscs was observed.

Article 16 of the Decree of 31 July 1923 (France) required that contaminated shellfish cannot be released to the public until after they have stayed 1 month in a depuration establishment. Since use of ozonized seawater can reduce this holding time to 24 to 48 hrs, the practical benefits of using ozone can be of great economic significance.

AQ-43

Title: "Sterilization of Seawater with Ozone: Application of This Method to the Purification of Contaminated Shellfish"

Author: H. Violle

Source: Rev. Hyg. et de Med. Preventive 51:42-46 (1929)

Reports a laboratory study to determine the effects of ozonized seawater to purify oysters. Samples of seawater, fresh water and distilled water (the latter 2 containing chloride, bromide and iodide in the same quantities as in seawater) were seeded with pathogenic bacteria (*B. typhus*, *B. coli*, *B. proteus*, *B. pyocaneus*, *cholera vibrio*, *B. dysenteria*) and the samples ozonized to determine the ozone dosages just necessary to attain disinfection. This dosage was the same in all cases (not given, but stated to be the same as for fresh water, which is 1 to 3 mg/l), and no oxidation of bromide was observed even at double the amount of ozone necessary to produce disinfection.

Oysters were kept 18 to 20 days in ozonized seawater using twice the ozone necessary for disinfection. The ozonized seawater was aerated to remove excess ozone. A second batch was kept in seawater. After 5 to 6 hrs the oysters in the ozonized water were free of bacteria. After 18 to 20 days exposure to ozonized water, there was no change in the oyster protoplasm.

Quantities of ozonized water used were 1 l/oyster/24 hrs, or 83 ml/oyster/hr, or 30 l/15 days/oyster, or 8,300 l/hr/10,000 oysters, or 14 l/min.

The ozone generator used was an Otto plate type unit. Neither the contacting apparatus, nor the ozone dosages, nor contact time were given.

The recommended depuration process consists of rapid sand filtration of seawater, ozonation, aeration, and flow through at the rate of 100 ml/hr/oyster.

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LITERATURE CITED -- BIOFOULING CONTROL (BF)

BF-01 Blogoslawski, W.J. & M.E. Stewart, 1976, "Marine Applications of Ozone Water Treatment", in Forum on Ozone Disinfection, E.G. Fochtman, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 266-276.

BF-02 Chase, R.E., 1975, "The Federal Water Pollution Control Act Amendments of 1972 -- PL 92-500 -- As It Relates to the Steam Electric Power Generating Industry", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 177-186.

BF-03 Garey, J., 1975, "Ozone For Anti-Fouling Control", presented at Workshop on Assessment of Technology and Ecological Effects of Biofouling Control Procedures at Thermal Power Plant Cooling Water Systems, Baltimore, Md., June 16-17. Electric Power Research Inst., Palo Alto, Calif.

BF-04 Garey, J., 1977, "A Comparison of the Effectiveness of Ozone and Chlorine in Reducing Slime Growth Within the Condensers of an Electric Generating Station Using Seawater as a Coolant", in Forum on Ozone Disinfection, E.G. Fochtman, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 277-283.

BF-05 Helz, G.R., R.Y. Hsu & R.M. Block, 1978, "Bromoform Production by Oxidative Biocides in Marine Waters", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 68-76.

BF-06 Mangum, D.C. & W.F. McIlhenny, 1975, "Control of Marine Fouling in Intake Systems - A Comparison of Ozone and Chlorine", in Aquatic Applications of Ozone, W.J. Blogoslawski and R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 138-153.

BF-07 Manning, G.B. & A.A. Bacher, 1975, "Ozone and the Steam Electric Power Industry", in Aquatic Applications of Ozone, W.J. Blogoslawski and R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 161-176.

BF-08 Senguta, C., G. Levine, E.C. Wackenhuth & C.R. Guerra, 1975, "Power Plant Cooling Water Treatment With Ozone", in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 119-137.

BF-09 Senguta, C. & R. Chakravorti, 1975, "Power Plants and Biofouling", Discussion, Workshop No. 4, in Aquatic Applications of Ozone, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 215-226.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BF-10 Siegrist, H.W., D.G. Tuttle & S.B. Majumdar, 1975, "Technical and Economic Considerations of Biocide System Options for Cooling Water Systems: A Review", in *Proc. Sec. Intl. Symp. on Ozone Technol.*, R.G. Rice, P. Pichet & M.-A. Vincent, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 632-649.

BF-11 Toner, R.C. & B. Brooks, 1975, "The Effects of Ozone on Four Species of Phytoplankton, Crab Zoea and Megalops and the Atlantic Silverside, *Menidia Menidia*," in *Aquatic Applications of Ozone*, W.J. Blogoslawski & R.G. Rice, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 154-160.

BF-12* Yu, H.H.S., G.A. Richardson & W.H. Hedley, 1977, "Alternatives to Chlorination for Control of Condenser Tube Bio-Fouling", EPA Report No. EPA-600/7-77-030, March. U.S. Environmental Protection Agency, Industrial Environmental Research Lab., Research Triangle Park, North Carolina 27711. NTIS No. PB-266,269.

BF-12

Title: "Alternatives to Chlorination for Control of Condenser Tube Bio-Fouling

Authors: H.H.S. Yu, G.A. Richardson & W.H. Hedley

Source: U.S. EPA Report # EPA/600/7-77-030 (March, 1977). Natl. Tech. Info Service, Report # PB-266,269/OWP.

Reports a study of methods used to lower free chlorine residuals in power plant effluents. Most U.S. power plants use chlorine (28,600 tons in 1972) to control biological fouling in their cooling systems, particularly in their condenser tubes. Using chlorine raises many questions regarding the toxicity of chlorinated compounds which may enter public drinking water systems or harm aquatic organisms in the receiving waters. The report considers viable alternatives to current chlorination practices used to decrease passage of ecologically harmful effluents to receiving waters.

Alternative methods include: use of other chemicals (BrCl, ClO_2, ozone, controlled release pesticides); more efficient methods of chemical application (serial dosing near the condenser inlet, adding dechlorination chemicals, blowdown timing control, chlorination by residuals feedback control); on-line mechanical cleaning (sponge ball system, brush system, hot water backflush system); and physical/chemical treatment. Information on advantages, disadvantages, costs and applicability for retrofit or new installations of these methods is presented. Promising approaches to reducing free chlorine residuals in power plant effluents are available.

LITERATURE CITED -- CYANIDES AND CYANATES (CY)

CY-01 Anonymous, 1974, Mitsui Shipbuilding Tech. Review 85:42-48 (Jan).

CY-02* Bahensky, V. & Z. Zika, 1966, "Treating Cyanide Wastes by Oxidation with Ozone." Koroze Ochrana Materialu 10(1):19-21. Chem. Abstr. 65:6907c (1966).

CY-03* Balyanskii, G.V., M.E. Selin & V.B. Kolychev, 1972, "Ozonation of Simple Cyanides in Water." Zhurnal Prikladnoi Khimii (J. Applied Chem.) 45(10):2152-2156.

CY-04* Besselievre, E.H., 1957, "The Economical and Practical Use and Handling of Chemicals Used in Industrial Waste Treatment". in *Proc. 12th Indl. Waste Conf.*, 342-363 (publ. 1958), Purdue Univ., Engrg. Bull. Ext. Serv. No. 94.

CY-05 Des Rosiers, P.E. & H.S. Skovronek, 1975, "The EPA Program and Industrial Advanced Wastewater Treatment Needs--Ozone", in *Proc. 1st Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 500-521.

CY-06 Diaper, E.W.J., 1972, "Ozone Moves to the Fore", Water & Wastes Engrg., May, p. 65-69.

CY-07 Eiring, L.V., 1969, "Kinetics and Mechanism of Ozone Oxidation of Cyanide-Containing Waste Water." Tstel Metal (USSR), 73-76.

CY-08* Fabjan, C. & R. Davies, 1976, "Decontamination with Ozone of Sewage Containing Cyanide", Wasser, Luft & Betrieb 20(4):175-178. Chem. Abstr. 85:148426u.

CY-09 Fabjan, C. & R. Davies, 1970-1977, "Die Reinigung Galvanischer und Anderer Abwasser nach dem Ozonizieren Verfahren", U.S. Dept. of Commerce, NTIS Report No. PS-77/0749.

CY-10* Fujisawa, T., Y. Matsuda, Y. Takasu, Y. Tanaka & H. Imagawa, 1973, "On the Ozone-Oxidation Treatment of Sewage Containing Cyanide or Cyanate." XXXI. Semi-Annual Autumn Mtg. of the Japanese Chemical Soc., Lecture 131, Oct.

CY-11 Guillerd, J. & C. Valin, 1961, "Traitment par l'Ozone", l'Eau, May.

CY-12 Garrison, R.L., C.E. Mauk & H.W. Prengle, Jr., 1974, "Cyanide Disposal by Ozone Oxidation". Final Report, U.S. Air Force Weapons Lab., Kirtland Air Force Base, New Mexico, Feb. Report No. AFWL-TR-73-212, U.S. Dept. of Commerce, NTIS Report No. AD-775,152/2WP.

CY-13 Ikehata, A., 1975, "Treatment of Municipal Wastewater by the Use of Ozone to Yield High Quality Water", in Proc. 1st Intl. Symp. on Ozone for Water & Wastewater Treatment., R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 227-231.

CY-14 Ishizaki, K., R.A. Dobbs & J.M. Cohen, 1978, "Ozonation of Hazardous and Toxic Organic Compounds in Aqueous Solution", in Ozone/-Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 210-226.

CY-15 Kandzas, P.F. & A.A. Mokina, 1968, "Use of Ozone for Purifying Industrial Wastewaters." Trudy Vses. Nauchno-Issled. in-ta Vodosnabzh., Kanaliz., Gidrotekh. Soouzhenii Imzh. Gidrogeol, 20:40-45. Chem. Abstr. 71:6388v (1969).

CY-16* Khandelwal, K.H., A.J. Barduhn & C.S. Grove, Jr., 1959, "Kinetics of Ozonation of Cyanides", in Ozone Chem. & Technol., Adv. in Chem. Series No. 21, Am. Chem. Soc., Washington, D.C. p. 78-86.

CY-17 Kolthoff, I.M. & V. Stenger, 1947, Volumetric Analysis, Vol. II, Interscience Publishers, New York, N.Y., p. 267.

CY-18 Kubo, A. & M. Nagata, 1974, "Highly Advanced Treatment of Water Treated by Activated Sludge Process Effluent of Gas Liquor." (Journal unknown)., Jan.

CY-19* Mathieu, G.I., 1973, "The Film Layer Purifying Process for Cyanide Destruction", Canadian Mining J., June, p. 3-4.

CY-20 Mathieu, G.I., 1975, "Application of Film Layer Purifying Chamber Process to Cyanide Destruction--A Progress Report," in Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 533-550.

CY-21 Mathieu, G.I., 1977, "Ozonation for Destruction of Cyanide in Canadian Effluents - A Preliminary Evaluation", Canada Centre for Mineral and Energy Tech., Ottawa, Canada, CANMET Report 77-11. Presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov. 1977. Intl. Ozone Assoc., Cleveland, Ohio.

CY-22 Matsuoka, H., 1973, "On the Ozone Treatment of Industrial Sewage", PPM 4(10):57-59.

CY-23 Neuwirth, F., 1933, Berg-u HÜttenmann. Jahrb. Montan. Hochschule Loeben, 81:126-131.

CY-24 Reznick, J.D., W.A. Moore & M.B. Ettinger, 1958, "Behavior of Cyanates in Polluted Water", Indl. Engrg. Chem. 50(1):71-72.

CY-25 Sondak, N.E. & B.F. Dodge, 1961, "The Oxidation of Cyanide-Bearing Plating Wastes by Ozone, Part 1", Plating, p. 173-180.

CY-26 Sondak, N.E. & B.F. Dodge, 1961, "The Oxidation of Cyanide-Bearing Plating Wastes by Ozone, Part 2", Plating, p. 280-284.

CY-27* Zumbrunn, J.P., 1971, "Produits et Procèdes--Epuration des Eaux Residuaires Cyanurées." Chimie et Industrie. Genie Chimique 104(20):2573-2584.

CY-02

Title: "Treating Cyanide Wastes by Oxidation with Ozone."

Authors: V. Bahensky & Z. Zida

Source: Koroze Ochrana Materialu, 10(1):19-21 (1966). Chem. Abstr. 65:6907c (1966).

The effect of Cu (as a catalyst) and pH on the oxidation of cyanides with ozone was investigated. CuCN and $CuK(CN)_2$ were oxidized rapidly, and the oxidation of NaCN, KCN, $Zn(CN)_2$, and $Cd(CN)_2$ was catalyzed with Cu 5 to 15 mg/l. The most suitable pH of the solutions for the oxidation was 10 to 11, because at lower pH HCN is liberated. A 500 mm column containing CN absorbed ozone satisfactorily. The method is suitable for treating cyanide wastes of higher concentration (minimum 100 mg/l).

CY-03

Title: "Ozonization of Simple Cyanides in Water."

Authors: G.V. Balyanskii, M.E. Selin & V.B. Kolychev

Source: Zhurnal Prikladnoi Khimii (Journal of Applied Chemistry) 45(10):2152-56 (1972).

Review: A study of the reaction of cyanide oxidation by ozone and of kinetic parameters. Data are presented, from which a schematic representation of the oxidation reaction is developed. CN ions are oxidized most rapidly, forming CNO ions, which are, in turn, oxidized to nitrate ions, and to carbonate and nitrogen. Overall consumption of ozone for the oxidation of CN ions to the final products under the experimental conditions was 5.8 to 6.0 moles/mole. The oxidation rate of CN and CNO ions conformed to a first-order equation with respect to these ions. The process was controlled by diffusion. The average value of the rate constant for the oxidation of CN ions (unit specific interfacial area) was 0.803/min; for CNO ions it was 0.157/min.

Contactor: In a thermostatic reactor (glass cylinder, 32 mm diameter and 400 mm height), 250 to 300 ml of a KCN-water solution were combined with the ozone-gas mixture at zero reaction time. At intervals its content was determined for CN, CNO, NO_3^- ions and ozone content.

Ozone Generator: Not described.

References: 16

CY-04

Title: "The Economical and Practical Use and Handling of Chemicals Used in Industrial Waste Treatment."

Author: E. H. Besselievre

Source: Proc. 12th Industrial Waste Conf., 1957, 342-63, Publ. 1958).
Purdue Univ. Engr. Bull, Ext. Serv., No. 94, Lafayette, Indiana.

Review: Lime, chlorine and chlorine-containing compounds, sulfur dioxide and ozone treatment for industrial wastes were analyzed from an economic point of view. Ozone costs were determined for the treatment of CN-containing wastes.

Economics: For daily wastes with a CN content of 160 lbs/day, the theoretical chlorine demand (1092.80 lbs/day) plus operating costs were estimated to total $130.25/day (1957 prices). Equipment for ozone generation (360 lbs/day) and use were estimated at an initial cost of $165,000. Using 2 lbs ozone/lb of cyanide, and with 13 kwhr of current needed to produce 1 lb of ozone, total daily costs are $111.46.

An alternative method, the use of "metered ozone", was studied. With the same ozone demands as above, charges paid to the owner of the ozone process equipment were determined to be $151.36/day. If 2000 lbs of cyanide/-day were to be treated, 4000 lbs of ozone at 17.5¢/lb would total $560.00. Comparable costs for chlorine use (7¢/day) would be $1120/day.

CY-08

Title: "Decontamination with Ozone of Sewage Containing Cyanide".

Authors: C. Fabjan & R. Davies

Source: Wasser, Luft & Betrieb 20(4):175-178 (1976). Chem. Abstr. 85:148426u.

The oxidation of CN^- and complex metallic cyanides with ozone in an alkaline medium is catalyzed by transition metal ions and is the basis of a treatment for wastewater containing CN^- and its complexes. By using a packed column and a countercurrent flow for the wastewater and ozone, the oxidation reaction was studied as a function of the concentrations of CN^- in the wastewater, of the ozone in the inlet gas and of the characteristics of the packed column. The concentration of ozone in the outlet gas also was determined and related to the parameters influencing the oxidation reaction. During wastewater treatment it was necessary to remove the heavy metal hydroxide sludge formed, because the sludge catalytically decomposed the ozone with a concomitant loss of the oxidizing agent. Based on the results obtained, plant design criteria are presented, and procedures are suggested for a continuous operation and for automation of the plant.

CY-10

Title: "On the Ozone-Oxidation Treatment of Sewage Containing Cyanide or Cyanate."

Authors: T. Fugisawa, Y. Matsuda, Y. Takasu & Y. Imagawa, II.,

Source: IXXX Seminannual Autumn Meeting of the Japanese Chemical Society, Lectures, p. 131, October 1973.

Solutions initially containing 350 mg/l of CN and 3 mole/l of CNO, respectively, obtained by dissolving pure KCN and KCNO, were reacted with a mixture of ozone and oxygen at 8.4 to 17.3 mg ozone/l in various states of pH controlled by adding NaOH. The reaction of CNO and ozone in alkaline solution followed the equation, $v = K[OH^-][O_3]$, and that CNO ion was oxidized to nitrogen.

CY-16

Title: "Kinetics of Ozonation of Cyanides."

Authors: Khandelwal, K.K., A.J. Barduhn & C.S. Grove, Jr.

Source: Ozone Chemistry & Technology, Advances In Chemistry Series, Vol. 21, American Chemical Society, Washington, D.C., 78-86.

Review: The rate of ozonation of an aqueous KCN solution was determined under controlled conditions using a packed tower and a bottle sparger as contactors. The effects of the following variables on the reaction rate were considered:

1) Cu(II) concentration from Cu sulfate. Addition of Cu(II) ions more than doubled the rate of decomposition of cyanides. Increasing the Cu(II) concentration did not markedly increase this further.

2) Cu(II) from other salts--cupric chloride, nitrate, acetate and sulfate. The presence of various anions had no effect on the reaction rate constant.

3) The manner in which ozone and cyanide interact--reactor bottle or packed column. There was no marked difference in the reaction rate constants, although that of the packed tower was slightly lower than that of the bottle. The controlling factor was the rate of reaction with CN. The rate of dissolution of ozone was very fast compared to the rate of its reaction with cyanide.

4) Cu(II), Ni(II), Mn(II), and Cd(II) sulfate. Cu(II) gave the highest rate constant (K = 2.20), followed by Ni(II) (K = 11.50), Mn(II) (K = 1.33) and Cd. The rate constant for Cd was nearly the same as for the uncatalyzed reaction (K = 0.95).

5) Solution temperature over 13°C to 30°C did not substantially affect the rate constant.

Ozone Generator: A Welsbach T23 Model laboratory ozone generator produced ozone from cylinder oxygen.

Contactor: Batch reactions were done in 2 types of reactors--a 1,500 ml packed tower and a 1,500 ml borosilicate glass bottle. Nearly all runs were conducted at 20° C with the pH maintained at 11.3 ± 0.5.

Economics: No cost assessments were made.

References: 9

CY-19

Title: "The Film Layer Purifying Process for Cyanide Destruction."

Author: G.I. Mathieu

Source: Canadian Mining J., June, 1973, 3-4.

Review: An explanation of the FLPC (Film Layer Purifying Chamber) contacting system.

Process: FLPC basically is the conventional ozone contact system in reverse. The aqueous solution is atomized and sprayed into a concentrated atmosphere of ozone and oxygen. This produces rapid oxidation (about 12 sec/reactor). The oxidized liquid is passed through an electric coagulator which removes SS and precipitates metal hydroxides. This is followed by sedimentation.

Discussion: Best results occurred with high concentrations of cyanides at a cost of 5 to 7 ¢/1,000 gal of 50 mg/l CN. Also discusses methods of reducing cost and improving efficiency. 91% to 97% of the CN was decomposed in less than 2 min using synthetic CN wastes.

References: None.

CY-27

Title: "Purification of Wastewaters Containing Cyanides"

Author: J.P. Zumbrunn

Source: Chemie et Industrie - Genie Chemique 104(20):2573-2584 (1971).

Reviews methods of treating cyanides. Ozonation is mentioned only and no experiments with ozone are described.

For conversion of CN to nitrogen and CO_2, excess ozone is required and the pH must be very alkaline.

$$CN^- + O_3 \rightarrow (CNO)^- + O_2$$

or:

$$2(CN)^- + 5O_3 + 2NaOH \rightarrow 2(NaHCO_3)^- + N_2 + 5O_2 + H_2O$$

References: 14

LITERATURE CITED -- ELECTROPLATING (EP)

EP-01* Anonymous, 1958, "Ozone Counters Waste Cyanides Lethal Punch", Chem. Engr., March 24, p. 63-64.

EP-02 Anonymous, 1974, "Ozonation: Another Way to Treat Plating Wastes", Prod. Finish 38:10, 98; Engrg. Index Monthly 12:049085 (1975).

EP-03 Anonymous, 1975, French Patent, FR 2,265,691 (Nov. 28). Derwent French Patent Abstracts x(3):D5, Feb. 1976.

EP-04 Bollyky, L.J., 1975, "Ozone Treatment of Cyanide and Plating Waste", in Proc. 1st Intl. Symp. on Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 587-590.

EP-05 Bollyky, L.J., C. Balint & B. Siegel, 1976, "Ozone Treatment of Cyanide and Plating Waste on a Plant Scale", in Proc. Sec. Intl. Symp. on Ozone Technol., R.G. Rice, P. Pichet & M.-A. Vincent, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 393-420.

EP-06* Bollyky, L.J., 1977, "Ozone Treatment of Cyanide-Bearing Plating Waste", EPA Report No. EPA-600/2-77-104, June. U.S. Environmental Protection Agency, Industrial Environmental Research Lab., Cincinnati, Ohio 45268.

EP-07* Browning, M.E., 1976, "Wastewater Treatment in the U.S.A", Galvanotechnik 67(6):465-470.

EP-08 Cheremisinoff, P.N., A.J. Perna & J. Ciancia, 1977, "Treating Metal Finishing Wastes, Part 2", Indl. Wastes Jan/Feb, p. 32-34.

EP-09* Ciancia, J., 1973, "New Waste Treatment Technology in the Metal Finishing Industry." Plating 60:1037.

EP-10 Ellerbusch, F. & H.S. Skovronek, 1977, "Oxidation Treatment of Industrial Wastewater", Indl. Water Engrg., Sept., p. 20-29.

EP-11* Fabjan, C., 1975, "Purification of Electroplating and Other Effluent Waters by the Ozone Process." Galvanotechnik 66(2):100-107.

EP-12 Fabjan, C., R. Davies & K. Marschall, 1970-1977, "Destruction of Complexing Agents in Electroplating and Other Effluents by Ozone", U.S. Dept. of Commerce, NTIS Report No. PS-77/0749, p. 643-645.

EP-13* Garrison, R.L., C.E. Mauk & H.W. Prengle, Jr. 1974, "Cyanide Disposal by Ozone Oxidation." Final Report, U.S. Air Force Weapons Lab., Kirtland Air Force Base, New Mex., Feb., #AFWL-TR-73-212, U.S. Dept. of Commerce, NTIS Report No. AD-775,152/2WP.

EP-14 Garrison, R.L., C.E. Mauk & H.W. Prengle, Jr., 1975, "Advanced Ozone Oxidation System for Complexed Cyanides." In Proc. 1st Intl. Symp. on Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 551-577.

EP-15* Garrison, R.L., H.W. Prengle, Jr. & C.E. Mauk, 1975, "Ozone-based System Treats Plating Effluent." Metal Progress 108(6):61-62.

EP-16* Goldstein, M., 1976, "Economics of Treating Cyanide Wastes", Pollution Engineering, March, p. 36-38.

EP-17* Ikehata, A., K. Ishizaki, N. Tabata & R. Hashimoto, 1972, "Oxidation of Cyanides in Plating Wastes by Use of Ozone." J. Japan Soc. for Safety Engr. II (2):74-84.

EP-18 Klingsick, G., 1975, "Application of Ozone at the Boeing Co., Wichita, Kansas", in Proc. 1st Intl. Symp. on Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 587-590.

EP-19 Kubala, F., 1964, "Regeneration of Chromium Bath with Ozone", Korose A Ochrana Materialu.

EP-20 Morquardt, K., 1973, "Treatment of Wastewater in the Metal Working Industry", Belg. Ned. Tijdschr. Oppervlakte Tech. Metal 16:306. Chem. Abstr. 81:63529 (1974).

EP-21 Pinner, W.L., 1952, "Progress Report of Am. Electroplaters Soc. Research Projects on Plating Room Waste", in Proc. 7th Indl. Waste Conf., Purdue Univ. Engr. Ser. 79:518-540.

EP-22 Prengle, H.W., Jr., 1977, "Evolution of the Ozone/UV Process for Wastewater Treatment", Presented at Seminar on Wastewater Treatment & Disinfection with Ozone, Cincinnati, Ohio, Sept. 15. Intl. Ozone Assoc., Cleveland, Ohio.

EP-23* Selm, R.P., 1959, "Ozone Oxidation of Aqueous Cyanide Waste Solutions in Stirred Batch Reactors and Packed Towers." In Ozone Chem. & Technol., Am. Chem. Soc., Adv. in Chem. Series, Vol. 21:66-67.

EP-24* Serota, L., 1958, "Science for Electroplaters 33. Cyanide Waste Treatment--Ozonation and Electrolysis", Metal Finishing, Feb., p. 71-74.

EP-25* Sondak, N.E. & B.F. Dodge, 1961, "The Oxidation of Cyanide-Bearing Plating Wastes by Ozone, Part 1", Plating, p. 173-180.

EP-26 Sondak, N.E. & B.F. Dodge, "The Oxidation of Cyanide-Bearing Plating Wastes by Ozone. Part 2", Plating, p. 280-284.

EP-27* Trejtnar, J., 1974, "Ozonization as a Means of Wastewater Purification", Czechoslovak Heavy Industry 10:34-35.

EP-28 Tyler, R.G., W. Maske, M.J. Westing & W. Mathews, 1951, Sewage & Indl. Wastes 23:1150-1153.

EP-29* Walker, C.A. & W. Zabban, 1953, "Disposal of Plating Room Wastes VI. Treatment of Plating Room Waste Solutions with Ozone", Plating, p. 777-780.

EP-01

Title: "Ozone Counters Waste Cyanide's Lethal Punch"

Author: Anonymous

Source: Chemical Engineering, March 24, 1958, p. 63-64

Describes the Boeing Aircraft (Wichita, Kansas) wastewater treatment facility serving the metal working plant.

Cyanide content in the 500 gpm influent ranges from 0.0 to 25 mg/l. Plant wastes first undergo oil separation, SO_2 reduction of chromates, alkaline precipitation of heavy metals and clarification. Treated wastes (at pH 9) pass through a contact tower packed with Intalox saddles, running countercurrent to air containing 1% ozone.

Liquid flow rate is 20,000 lbs/sq ft/hr; total air flow rate is 120 cu ft/min. Liquid effluent from this tower is acidified to pH 7 (carbonation), clarified, then passed through a second packed column countercurrent to the gaseous flow from the first tower, which still contains some ozone.

This double pass technique ensures complete oxidation of cyanide to cyanate and beyond, and also removes any excess SO_2 present from the chromate step. After ozonation, cyanide content of the effluent is below the limit of detection (0.1 mg/l).

Ozone Generators: Two 60 lb/day (from air feed) Welsbach generators.

Costs: For 120 lbs/day: $70,000 installed (about $600/lb of ozone generation capacity) including auxiliaries; operating costs: 14 to 15¢/lb of ozone (1958 prices).

Ozone is considered to be cost-effective over chlorine when the accessories needed to support chlorination (large detention basins, facilities for chemicals handling and storage, a gas-tight room for chlorinators), railway spurs for moving chlorine cylinders, dechlorinating equipment, etc.) are considered. Also, chlorination of cyanide produces 8 to 15 parts of chloride/-part of CN eliminated, and this fact must be considered in discharge of treated effluents.

EP-06

Title: "Ozone Treatment of Cyanide-Bearing Plating Waste"

Author: L. J. Bollyky

Source: EPA Report No. EPA-600/2-77-104, June, 1977. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

A plating waste treatment plant was installed at the Sealectro Corp, Mamaroneck, New York, to demonstrate the effectiveness of ozone treatment for the oxidative destruction of cyanides and cyanates and for the removal of Cu and Ag oxides on a full plant scale. The treatment process was designed to treat wastewaters from Cu, Au and Ag plating operations. A 9-month study was carried out to evaluate the effect of process parameters, to identify and optimize key parameters, to establish capital and operating costs, and to produce an effluent meeting current discharge standards.

Wastewaters: The Sealectro plant plates about 2.6 sq m/hr (1200 amps capacity) and produces 2 wastewaters: an *acid wastewater* (16 gpm, with surges to 24.6 gpm), containing Ni up to 14 mg/l, Sn up to 10 mg/l and Pb up to 0.08 mg/l; and an *alkaline CN wastewater* (6.75 gpm, with surges to 10.4 gpm), containing up to 60 mg/l CN, up to 32 mg/l Cu and up to 3.4 mg/l Ag. The combined flow averages 34 gpm, with surges up to 50 gpm.

Process: Alkaline CN wastewater is ozonized and the ozonate sent to a flash mixing tank where it is mixed with the acid wastewater stream. The pH is adjusted by addition of caustic or sulfuric acid (controlled by pH monitor), then discharged to a settling tank (50 min retention time). The clear effluent is discharged to the sewer system.

Ozone Generator: A 20 lb/day (from air) PCI Ozone Corp. generator which can be fitted with an auxiliary air blower to increase production to 26 lbs/day.

Contactor: A cylindrical, 2-compartment fiberglass tower 5.6 m (18.5 ft) tall and 0.8 m (30 inches) in diameter. Total volume 2,250 liters (600 gal). In the lower compartment are porous tube spargers for treating the alkaline CN-containing wastewater. In the smaller, upper compartment, off-gases from the lower compartment are reintroduced into the incoming alkaline wastewater, and either are passed through a packed column (sprayed with incoming alkaline CN-containing wastewater, or diffused into incoming wastewater. In this manner nearly all ozone introduced is utilized. Vent off-gases from the ozone contactor consistently contain <0.05 ppm (by volume) of ozone.

Results: The plant was designed in 1968 to meet the following local wastewater discharge standards: pH 5.5-9.5, 65°C (max), Cu 3.0 mg/l, CNO 10.0, CN 1.0, Ni 10.0, Ag 0.05, Cl 100.0 mg/l. To meet the current EPA BPTCA monthly average heavy metal discharge standards (based on 80 l/sq m flow and 30 day average maximum discharge rates): CN oxidizable by chlorine 0.1 mg/l, total

CN 1.0, Cu 1.0, Fe 2.0, Pb 1.0, Ni 1.0, Ag 0.1, Sn 2.0, Zn 1.0, TSS 40.0 mg/l, pH 6.0-9.5 (average daily discharge). The plating plant uses 1,200 amps only for plating and falls under local discharge standards.

To meet the current discharge standards requires ozone dosages of 1.85 to 2.8 mg/l of ozone per mg/l of CN (1.0 to 1.5 mole ozone/mole CN) at an initial alkaline CN wastewater pH of 7.0 to 9.5. Final effluent from the settling tank has a pH of 9.0 to 9.5 and temperature of 14° to 20°C. The effluent wastewater consistently contains 0.08 mg/l CN, 6 mg/l CNO, 1.7 mg/l Cu, 0.4 mg/l Ni and <0.1 mg/l Ag. $[CNO^-]$ can be reduced even further by additional ozone, but this is not required by the current discharge standard.

The amount of ozone required depends upon the initial $[CN^-]$. Below 20 mg/l of CN^-, the mole ratio of ozone/CN is 1:1 to reduce $[CN^-]$ to <0.1 mg/l. Concentrations of 20 to 40 mg/l CN^- require 2:1 to obtain <1 mg/l CN^- and 3.6 to attain < 0.1 mg/l CN^-. Above 50 mg/l CN^-, a mole ratio of 1.33 ozone/CN is required to obtain 0.52 mg/l CN^- in the effluent, but CNO^- discharge requirements are not met. The pH is not critical; the standards are met consistently over the range of 7 to 13.

Plant scale studies of ozonation of NaCN solns showed that at mole ratios of 2.65 ozone/CN, 97.6% of the CN was destroyed. Mole ratios of 4.3 removed 44.8% of the CNO and mole ratios of 14.0 removed 97% CNO.

For Cu cyanide solutions, 1 to 1.5 moles ozone/mole of CN reduces $[CN^-]$ to <0.1 mg/l at $[CN^-]$ up to 20 mg/l. As $[CN^-]$ increases to 75 mg/l, the mole ratio of ozone/CN rises to 3.0 to meet the discharge standard.

Costs: The optimum treatment process (described above) operated 24 hrs/day is estimated (capital + operating, 1975 prices, 15 yr amortization) to cost $1.31/1,000 gal of combined plant wastewater. Capital investment for this optimized system is estimated at $51,200. With increased ozone dosages (up to 2 moles ozone/mole CN), plus the addition of flocculant or settling tubes in the settling tank, the effluent water could be used to cool the ozone generator or air conditioning equipment.

In 2 weeks of operation, only 1 to 2 kg of sludge is produced in the settling tank.

EP-07

Title: "Wastewater Treatment in the USA"

Author: M.E. Browning

Source: Galvanotechnik 67(6):465-470 (1976)

Reviews wastewater treatment techniques for electroplating wastes in the USA. Use of ozonation for destruction of cyanides and removal of heavy metals is mentioned. Boeing Aircraft Co. has been using 55 to 160 kg/day of ozone for cyanide destruction since 1957.

References: 29

EP-09

Title: "New Waste Treatment Technology in the Metal Finishing Industry."

Author: J. Ciancia

Source: Plating, October, 1973, 1037-42.

Review: Reviews current technologies in the treatment of plating wastes, one of which is ozone. No experimental data are reported.

Oxidation of CN^- to CNO^- by ozone is rapid and practically instantaneous in the presence of a trace of Cu, but oxidation of CNO^- is slow. However, hydrolysis can convert CNO^- to ammonium ion.

Ozonation adds no salts or toxic constituents to the wastewater. The U.S. EPA is sponsoring a full scale demonstration study (see EPA-600/2-77-104) of the use of ozonation to destroy CN^- in plating wastewaters to determine the effectiveness of treatment and establish capital and operating costs of the process.

References: 1.

EP-11

Title: "Purification of Electroplating and other Effluent Water by the Ozone Process."

Author: C. Fabjan

Source: Galvanotechnik 66(2):100-107 (1975)

Review: Reviews various uses of ozone for purification of galvanic and other wastewaters. Ozone was efficient in the detoxification of CN-containing galvanic wastewater, reacting with CN^- to form CNO^-. The CNO^- was further hydrolyzed to CO_2 and NH_4^+ at low pH values. Ozone is used on a full scale for the treatment of wastewaters containing cyanides, phenols, oil residues, detergents, sulfides, sulfites and for the oxidation of Fe and Mn compounds, as well as nitrates.

Nitrogen, CO_2, ammonium carbonate and urea are formed during ozonation of CN-containing wastewaters. It was recommended that ozone be generated from oxygen rather than air for treatment of concentrated CN^- solutions.

CN^- concentrations of 20 to 100 mg/l were studied. At pH 10, 3 vol % ozone in air (2 l/hr) reduced 50 mg/l KCN to below 10 mg/l in 12 min. At pH 12, the CN^- level was reduced to below 0.1 mg/l in 12 min. Under the same conditions, Cu complex cyanides were destroyed faster (less than 10 min). 1 mole of CN^- requires 1 mole of ozone for destruction in 20 to 30 min.

Contacting: is not discussed.

Economics: In the U.S. the cost of ozone production is figured at around 16 and 7¢/kg, depending on whether ozone is produced with air or oxygen. These numbers show that, in some cases, the use of ozone instead of Cl_2 or OCl^- is more economical.

The capital expense should amount to $1,000 to $2,000/kg generated per day (oxygen or air, respectively). With rising capital cost of the plant, operating expenses decrease. Production of ozone represents 75% of the total cost of operation.

Efficiency: 1 kg of ozone is produced with an energy expense of 8 to 20 kwh at a concentration of 20 to 30 g/cu m of air. The use of oxygen instead of air reduces the specific energy consumption by half while ozone capacity is increased 2 to 3 times.

References: 20

EP-13

Title: "Cyanide Disposal by Ozone Oxidation"

Authors: R.L. Garrison, C.E. Mauk and H.W. Prengle, Jr.

Source: AFWL Report TR-73-212. Final Report for Period April 1972-Nov. 1973 (Feb. 1974). U.S. Air Force Weapons Laboratory, Kirtland Air Force Base, N. Mexico 87117

Review: A process was developed for complete destruction of total CN^- in influents as high as 100,000 mg/l, or below 1 mg/l, to produce effluents with total CN^- below the limits of detection. Influents were aqueous CN^- and complexed metal CN^- wastes from Air Force electroplating operations and color photographic film processing.

Laboratory studies showed that destruction of concentrated CN^- is limited by mass transfer of ozone, and destruction of dilute CN^- is limited by chemical reaction rate. Ozone at slightly elevated temperatures in the liquid (150°F) was more effective than ozone alone, but ozone with UV light was effective enough to permit design of a successful system. A 4 watt, 253.7 nm UV bulb, submerged in the liquid in the reactor, was the UV source.

A pilot scale prototype was designed, constructed and operated to destroy CN wastes to below the detectable limit. The conceptual design of a full scale system is included.

Wastewaters Studied: included Ni stripping, Cu plating, Cd plating, photographic bleach and photographic fixer, each treated by UV/ozone in low and high concentrations. In all cases, total [CN^-] in the effluents was below the detectable limit.

Experimental Details: Acrylic plastic was used for the reactor (it is transparent) and stainless steel and Al were used for portions of the system in contact with the dry gas phase. Synthetic wastes were studied first. Ozonation at pH 11.0 converted all CN^- to CNO^-, after which acidification to pH 4 immediately hydrolyzed CNO^-. Three lbs of ozone were found to react with 1 lb of free CN, except for Cu-containing solutions, in which the ratio was 2.5/1. Similar results were obtained using actual plating and photoprocessing wastes.

Prototype Reactor: 3 vertical countercurrent contact stages were used, each containing UV light sources and 420 RPM agitation. UV light was used only when the [CN^-] was expected to be <50 mg/l or when Fe cyanide complexes were present. The prototype was designed to treat 0.5 gal/8 hrs of waste containing 40,000 mg/l CN^-, or 15 gal/24 hrs of waste containing 4,000 mg/l CN^-, or lower.

Each contacting stage was 12 inches in diameter and 16.5 inches tall. Six 15-watt tubular UV lamps (253.7 nm) were mounted vertically in each stage, 1 inch from the reactor sidewalls. A W.R. Grace LG-2-L2 ozone generator (oxygen feed) was used, producing 3.2% (by weight) ozone.

Prototype Results: With dilute CN^- wastes (photo bleach, photo fixer, Cu plating and Ni strip) containing 10 mg/l CN^-, at waste feed rates of 20 gal/day and UV lamps on in all 3 reactor stages, no CN^- was detectable in the 2nd or 3rd stages for any runs.

Four additional runs were made on concentrated wastes. For Cu plating waste, UV and heat (150°F) were used in the 3rd stage only (ozone only in the 1st and 2nd stages). The liquid feed contained 4,000 mg/l CN^- (pH 11.5); pH in stage 3 was controlled at 7 to 8 using sulfuric acid; the effluent contained below 0.1 mg/l CN^-. 2.4 wt % ozone was fed to the 3rd and 2nd stages (0.14 lb/day and 1.96 lbs/day, respectively) and off-gases from these stages were fed to the 1st stage (2.1 lbs ozone/day total). Approximately 1,600 mg/l of SS were formed. Over 99.5% of the CN^- was destroyed in the 1st stage, leaving only Fe-complexed-CN^-.

Ni strip (4,000 mg/l CN^-) was treated similarly with similar results. (0.16, 0.26 and 1.68 lbs/day of ozone were fed to the 3rd, 2nd and 1st stages, respectively. 97% to 99% of the CN^- was removed in the 1st stage. The treated effluent contained 130 mg/l SS.

With photo fixer (700 mg/l CN^-), 0.43, 0.43 and 1.23 lbs/day of ozone were fed to the 3rd, 2nd and 1st stages, respectively. UV was used in stage 3 only, but 150°F was maintained in all 3 stages. pH in stage 1 was controlled at 7 with NaOH. [CN^-] was reduced to 550 mg/l in stage 1, to 70 mg/l in stage 2 and to <0.2 mg/l in stage 3. Treated water contained 625 mg/l SS.

Photo bleach (4,000 mg/l CN^- complexed with Fe) was treated in 6 stages and 5.9% ozone was employed. 0.50, 0.38, 0.38, 0.50, 0.38 and 0.38 lbs/day of ozone were fed to the 6 successive stages. UV was used in stages 5 and 6, and 150°F was maintained in all stages. [CN^-] leaving the 6 successive stages, respectively, were 2,680, 1,630, 710, 105, 13 and <0.3 mg/l. About 1,900 mg/l SS were produced.

In all 4 concentrated wastewater runs, 93% to 99% of the CNO^- also was destroyed.

Cost Estimates: A 3-staged system to treat 5 gpm of cyanide (50,000 mg/l total CN^-), allowing 10.7 hrs/contact stage and using UV and pH control in the 3rd stage only, and 7,560 lbs/day of ozone (from oxygen) is estimated to cost $2.5 MM (plus liquid oxygen storage) and will use 1.35 megawatts of electricity. This unit would operate 24 hrs/day - 7 days/week.

For treating 1,000 gal/week in 5 24-hr days, ozone (210 lbs/day) would be generated from air and the installed cost is estimated at $217,000. Operating costs would be 8 man hrs/week, 60 Kw of electrical power and $5,000/yr replacement UV lights.

EP-15

Title: "Ozone-based System Treats Plating Effluent."

Authors: R.L. Garrison, H.W. Prengle, Jr. and C.E. Mauk

Source: Metal Progress 108(6):61-62 (1975).

Describes the advantages of treatment of CN compounds with a combination of ozone with a small amount of UV light over alkaline chlorination. Cyanides are destroyed to below the limit of detection in multi-staged ozone/UV reactors. After oxidation, the pH is adjusted to 10 with alkali, followed by precipitation of all heavy metals in a settling tank. >80% of the treated water is recycleable, saving rinse water cost.

First cost of ozone/UV equipment is comparable to that of chlorination, but operating costs are substantially less. These are not cited.

EP-16

Title: "Economics of Treating Cyanide Wastes."

Author: M. Goldstein

Source: Pollution Engineering, March 1976, 36-38.

Review: The cost factors of various methods of CN^- waste treatment were discussed. Included were the processes of chlorination by Cl_2 gas and NaOCl, oxidation by $KMnO_4$, H_2O_2, wet air oxidation, activated carbon treatment and ozonation.

Economics: Ozone treatment was practical for partial destruction of 20 lbs of CN^-/day, or for total destruction of 10 lbs/day. The generator would cost about $30,000 with annual operating costs being $1,200, vs $6,000 to $10,000/yr operating costs for Cl_2 gas treatment (Table 4).

Efficiency: Only 40% as much ozone is needed as Cl_2 gas to oxidize each lb of CN^-.

TABLE 4. COST COMPARISONS OF TREATING CYANIDE WASTEWATERS BY A VARIETY OF TECHNIQUES

Treatment Process	Cyanide Treatment Rate	Capital Costs	Operating Costs
Cl_2 gas	5 lbs/hr	$15,000-30,000	$0.75-1.00/lb CN to CNO $1.50-2.00/lb($6000-10,000/year) CN completely destroyed
NaOCl	4-5 lbs/hr	$75,000-90,000	2.5 kwhr ($2.00/lb CN to CNO)
$KMnO_4$	5 lbs/hr	$15,000-30,000	$6.00/lb CN to CNO/@40¢/lb of $KMnO_4$
H_2O_2	100-1000 ppm as NaCN	not estd.	$1.50/lb CN to CNO followed by acid hydrolysis
Wet Oxidation	2000-4000 mg/l	not estd.	nearly complete CN removed in 5 acrylonitrile plants
Activated Carbon	20 gpm (1 lb CN/hr)	$45,000	$6.00/lb of CN destroyed, assuming no regeneration. Carbon must be replaced every 4 days
Ozone	20 lbs/day to CN or 10 lbs/day totally destroyed	$30,000	$1,200/yr

EP-17

Title: "Oxidation of Cyanide in Plating Wastes by Use of Ozone"

Authors: A. Ikehata, K. Ishizaki, N. Tobata & R. Hashimoto

Source: J. Japan Soc. Safety Engrg. II(2):74-84 (1972)

Batch and continuous run tests were conducted on Ag and Cu plating wastes.

Ozone Generator: Mitsubishi Electric Corp. tube-type, producing 70 g/hr ozone from dry air. Oxygen was used to produce ozone for the batch tests; air for the continuous tests.

Contactor: Sparger for batch tests in a vessel containing 300 ml of sample. For continuous run tests, a circulating type ejector. Flow rate of wastewater: 3.6 cu m/hr. Ozonized air flow: 4.8 cu m/hr. 3rd and 4th stage contacting in series was preferable so as to complete decomposition of CNO^-.

Results: CN^- is decomposed and CNO^- is generated soon after ozonation begins. CNO^- decomposes upon further ozonation. Decomposition of CNO^- starts when total $[CN^-]$ becomes about 60 mg/l (Cu plating wastes) and about 5 mg/l (Ag plating wastes). Ferrous CN complex is the most difficult to be decomposed, whereas Ni and Cu complexes are decomposed rapidly.

Ozone consumption increases considerably as $[CN^-]$ decreases. Rate of ozone decomposition was zero order between pH 6 and 8, 1st order with respect to CN^-, and 0.5th order with respect to $(OH)^-$.

Unreacted ozone should be recycled (increasing its absorption efficiency to 95%) and any excess destroyed by feeding into a boiler combustion chamber or absorption onto activated carbon.

For complete decomposition of CN^- by alkaline chlorination, 6.82 moles of Cl_2 theoretically are necessary/mole of CN^-, but practically, large excesses are required and the pH must be kept at 9 or above. However, cyanic acid decomposition occurs rapidly only at pH 6.5 to 7. Thus alkaline chlorination requires 2-stage pH control.

On the other hand, ozonation of either CN^- or CNO^- can be done under nearly neutral conditions. The CN/ozone mass ratio for 1st stage oxidation is 0.542; for 2nd stage decomposition (of CNO^-) 0.217. In acidic solution, the CN/ozone mass ratio for 2nd stage decomposition of CNO^- is 0.361.

The biggest drawback of ozonation is equipment costs. Present generating costs are 200 yen/kg, including depreciation of equipment. Ozonation of CN^- wastes thus is somewhat less costly than alkaline chlorination.

EP-23

Title: "Ozone Oxidation of Aqueous Cyanide Waste Solutions in Stirred Batch Reactors and Packed Towers."

Author: R.P. Selm

Source: Ozone Chemistry & Technology, Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D.C., 66-77 (1959).

Review: Methods of treatment of CN^- wastes are reviewed, comparing the efficiency and costs of ozone oxidation with those of Cl_2 use, with emphasis on pH factors and on the use of redox potential in the control of ozone addition. In the ozonation of cyanides there is an extremely rapid absorption of ozone, with no ozone being in solution during this phase ($CN + O_3 \rightarrow CNO^- + O_2$). The redox potential is at a low value, rising slowly as the CN^- is consumed, but rises suddenly when the CN^- has been practically completely oxidized. The pH is lowered as CN^- is oxidized. As the pH falls, the amount of free CN^- decreases rapidly; at the end of ozonation the CN^- is almost exclusively present as hydrocyanic acid, with a neutral pH.

Ozone is more soluble in acid than in alkaline solutions, dissolving in dilute acid with a rapid rise in pH as long as the pH is <10.5. The pH returns to the original level as ozone decomposes. The reaction is controlled by mass transfer. The presence of some metals, particularly Cu, appears to speed up the reaction. CN requirements are between 1 and 0.33 moles of ozone/mole of CN^-.

In the laboratory, ozone oxidized ferrocyanides first to ferricyanates and then to ferric hydroxide sols. Traces of ferricyanide remained even after prolonged ozonation, as did some ferrocyanide ions. 39% of the total flow of ozone was absorbed. A ratio of 7.25/1 moles of ozone absorbed:mole of $K_4Fe(CN)_6.3H_2O$ was found, including the ozone decomposed by catalysis due to hydroxyl ion and other causes.

The redox potential of ozonized distilled water decayed at an approximately linear rate on a plot of millivolts vs log time. The decay was much faster for solutions containing ozone demand, and was roughly proportional to the amount of the ozone demand.

Packed tower studies indicated that ozone may react on the basis of 0.33 mole of ozone/mole of CN^-.

Ozone Generator: Ozone was generated by a Welsbach T23 lab ozonator fed with oxygen. 0.12 cu ft/min of ozonized oxygen at 70° F and 8 psig were fed to the reaction system.

Contacting: For batch solutions, a 3.5 l ceramic vessel with a variable speed, all-glass tubing agitator, and fritted glass diffusion bulb at the bottom was used for the ozonation at atmospheric pressure. Packed tower studies were made with a borosilicate glass column 4 inch I.D. and 4 ft long, packed with 0.25 inch ceramic Intalox saddles. The feed was distributed through the tower with a perforated aluminum plate. Feed solution flow rates were increased to as high as 30,000 lbs/sq ft/hr, with ozone at 1.78% by wt. Each soln was held at least 15 min.

Economics: Chlorine costs depend on plant location and size, and vary from 15¢ to 3¢/lb. Ozone costs vary directly with the cost of electrical power, and are about 13¢/lb, based on 1¢/kwhr (1957 prices).

References: 24

EP-24

Title: "Science for Electroplaters 33. Cyanide Waste Treatment--Ozonation and Electrolysis."

Author: L. Serota

Source: Metal Finishing 56:71-74 (1958).

Solutions representing waste Cu and Zn cyanide plating solutions were prepared. Ozone was prepared from air previously dried by passing through sulfuric acid and anhydrous $CaSO_4$. However about 0.1% (by vol) N_2O_5 was present. The contactor was a 500 ml bottle, with a sintered glass tube.

Cu or Mn(II) at 10 to 20 mg/l were necessary for the quantitative oxidation of 200 mg/l of CN^- to CNO^-. Without Cu or Mn, only 40% to 60% of the ozone added reacted with CN^-. Cu plating solns did not require a catalyst. The ratio of ozone/CN^- varied between 1.05 and 1.57.

CN^- radical in a ferrocyanide compound is not oxidized by ozone.

An appreciable drop in pH resulted in most of the runs. A pH >10 was recommended as a safeguard against HCN volatilizing. Oxidation of CN^- to CNO^- is instantaneous, and the pH range for effective oxidation is 7 to 12.5. Hydrolysis of CNO^- to NH_4^+ can be effected by lowering the pH to about 3.

Ozonation is satisfactory for large volumes of solutions with concentrations <5 mg/l of CN^-, since the $[CNO^-]$ formed would be <10 mg/l, which is below the toxic concentration.

EP-25

Title: "The Oxidation of Cyanide-Bearing Plating Wastes by Ozone. Part I"

Authors: N.E. Sondak & B.F. Dodge.

Source: Plating (1961) 173-80.

Review: This was a study of the system variables required to design an adequate ozone-CN waste disposal unit. The variables tested were:

(1) Flow rate of ozonized air through the solution: 0.024 to 0.084 cu ft/min.
(2) Inlet ozone concentration: 4.29 to 45.2 mg/l.
(3) Solution constituents: pure aqueous CN^- solution, synthetic and actual plating solutions, and pure aqueous solution.
(4) Operating temperature: 25.9° to 30.6°C.
(5) Solution pH: (initial) 10.3 to 12.4.
(6) Possible catalysts: Cu, Mn, V and Fe salts at concentrations of 1 to 10 mg/l.
(7) Effect of reactor geometry: the ratio of liquid depth to reactor diameter.

Results indicated that the reaction between ozone and CN^- follows the equation:

$$CN^- + O_3 \rightarrow CNO^- + O_2$$

with the rate-controlling step being the mass transfer of ozone. Raw data are presented with no interpretation.

Ozone Generator: Dry air ozonized in a Welsbach T-23 lab ozonator.

Contactor: Nitrogen oxides were removed from the ozonized air mixt by passing through dilute NaOH solution. The ozone concentration was measured, the solution then being sent to a Pyrex column reactor, 4 ft by 2-3/8 inches I.D., which was usually operated two-thirds full. From here exiting gases were run through an ozone-absorption system, metered by a wet-test meter. Assays were done for CN^-, CN plating solutions, CNO^- and Cu plating solutions.

Economics: Specific cost data are not presented.

References: 6

EP-27

Title: "Ozonization as a Means of Wastewater Purification."

Author: J. Trejtnar

Source: Czechoslovak Heavy Industry 10:34-35 (1974)

Review: The technology of ozone removal of cyanides from metal surface finishing wastewaters was tested at the Water Conservancy Research Institute and at the Chemical Equipment Research Institute, both of Brno, Czechoslovakia.

Ozone was used to oxidize substances to be neutralized, as well as materials such as Fe(II), manganous salts, H_2S or nitrates. There was a 2-step reaction between ozone and cyanides:

$$2KCN + 2O_3 \rightarrow KCNO + 2O_2$$

$$2KCNO + H_2O + 3O_3 \rightarrow KHCO_3 + N_2 + 3O_3$$

About 1.1 to 1.6 volumes of ozone were required for 1 volume of CN^- to be oxidized to CNO^-. Purified water could be recirculated as service water.

EP-29

Title: "Disposal of Plating Room Wastes VI. Treatment of Plating Room Waste Solutions with Ozone."

Authors: C.A. Walker & W. Zabban

Source: Plating 777-780 (1953).

Review: A second paper on removal of CN^- from plating waste solutions, the first being on Cl_2 and OCl^- use. Attention was given to the ability of ozone to oxidize CN^- ions in plating wastes to cyanates. Oxidation of the free and complex CN^- ions by ozone was instantaneous, resulting in the formation of free cyanates, soluble metallic cyanates and hydroxides. The reaction required a catalyst (Cu in the sulfate form and Mn(II) were used) if the solution did not contain metals known to be oxidation catalysts. If no catalyst was present when treating NaCN and Zn, large amounts of unreacted ozone would leave the solution; a catalyst was not required for the Cu plating solutions.

Ozone requirements varied from 1.1 to 1.6 lbs/lb of reacted CN^-.

Ozone Generator: Ozone was produced by an apparatus constructed in the project lab, using dried air. It consisted of a glass tube with tin foil and the usual electrical accessories. It was not water-cooled. A 1.2 volume % concentration of ozone was generated.

Contactor: The reaction vessel was a 500 ml, wide-mouthed bottle. The ozone-air mixture was bubbled through a sintered glass tubing and then through the reactor. A 5% aqueous KI solution was used to measure the amount of unreacted ozone.

Economics: Information on cost was not included.

References: 12

LITERATURE CITED -- FOOD & KINDRED PRODUCTS (FO) & BREWING (BR)

FOOD & KINDRED PRODUCTS (FO)

FO-01 Barrett, F., 1970, "Minimizing the Waste Disposal Problem in Vegetable Processing." Proc. Symp. Farm Wastes. The Institute of Water Pollution Control & the Univ. of Newcastle-upon-Tyne (8):57-65.

FO-02* Coffre, R., 1931, "Process for Ozonization of Fermented Liquids", English Patent 340,647, January 8. Abstracted in J. Inst. Brewing, London (1931), p. 449.

FO-03 Leavitt, P. & J.V. Ziemba, 1969, "At Gerber Water Does Triple Duty", Food Engrg. 41:90-91.

FO-04* Leavitt, P., 1972, "Water Reuse Through Ozone Sterilization", ISA FID-726,408, p. 19-24.

FO-05 Netzer, A., M.J. Riddle, I.J. Marvan & S.G. Nutt, 1977, "Use of Ozone for Disinfection of Salmonella in Poultry Plant Effluent", presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov. Intl. Ozone Assoc., Cleveland, Ohio.

FO-06 Rivkowich, H., W.C. Rehman, W. Knapp & B. Borders, 1974, "Method of Extracting Tea", U.S. Patent 3,809,769, 3 May. Chem. Abstr. 81:90130 (1979).

FO-07* Walter, R.H. & R.M. Sherman, 1974, "Ozonation of Lactic Acid Fermentation Effluent." J. Water Poll. Control Fed. 46(7):1800-1803.

FO-08* Walter, R.H. & R.M. Sherman, 1976, "Efficiency of Oxygen Demand Reduction of Sauerkraut Brine by Ozone." In *Proc. Second Intl. Symp. on Ozone Technology*, R.G. Rice, P. Pichet & M.-A. Vincent, Editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 694-698.

FO-09 Yim, B., R.H.F. Young, N.C. Burbank, Jr. & G.L. Dugan, 1975, "Bakery Waste: Its Characteristics & Treatability. Part I", Indl. Wastes, March/April, p. 24-25. Part II, *Ibid*, Sept/Oct., p. 41-44.

BREWING (BR)

BR-01 Coffre, R., 1931, "Process for Ozonisation of Fermented Liquids", British Patent 340,647, Jan. 8. Abstracted in J. Inst. Brewing (London), p. 449 (1931).

BR-02* Du Jardin, E., 1924, "The Application of Ozone in the Brewery", Ann. Brass. et Dist. 23:122. Abstracted in J. Inst. Brewing, London (1925), p. 88.

BR-03* Fergason, R.R., H.L. Harding & M.A. Smith, 1973, "Ozone Treatment of Waste Effluent", Research Technical Completion Report, OWRR Project No. A-037-1 DA, Water Resources Research Inst., Univ. of Idaho, April. U.S. Dept. of Commerce, NTIS Report No. PB 220,008.

BR-04* Geminn, C.C., 1974, "Concentrated Wort Processing Method", Master Brewers Assoc. of America, Tech. Quarterly 11(1):21-25.

BR-05* Mayrhofer, K.G. & H. Steinhardt, 1955, "Use of Ozonized Water in Yeast Manufacture", Brauwelt, 857-859. Abstracted in J. Inst. Brewing, London 61:530 (1955).

BR-06* Schäuble, R. & M. Gillardin, 1958, "Ozonized Water in the Brewing and Mineral Water Industries", Brauerei, Wissenschaft Beil. 11:75-86. Abstracted in J. Inst. Brewing, London 64:515 (1958).

BR-07* Tenney, R.I., 1973, "Ozone Generation and Use in the Brewery", Brewer's Digest 48(6):64-66.

BR-08* Tenney, R.I., 1973, "Ozone, the Add-Nothing Sterilant", MBAA Technical Quarterly 10(1):35-41.

BR-09* Van Laer, M., 1928, "The Use of Ozone in Brewing", Petit J. Brass. 36:854-856. Abstracted in J. Inst. Brewing, London, p. 497 (1928).

FO-02

Title: "Process for Ozonization of Fermented Liquids."

Author: R. Coffre

Source: English Patent 340,647, January 8, 1931. Abstracted in J. Inst. Brewing, London, (1931), p. 449.

Describes a process to accelerate the natural aging of wines and spirits without formation of bad flavors. A metal vat is packed with wicker baskets of oak chips which are ozonated and alternately soaked with the fermented liquid. This avoids any taste problems associated with direct application of ozone to the fermented liquid.

This process is claimed to create the same aged qualities observed in liquids aged 10 to 15 yrs by means of 15 to 20 soakings at intervals of 24 hrs.

FO-04

Title: "Water Reuse Through Ozone Sterilization"

Author: P. Leavitt

Source: Instrumentation in the Food & Beverage Industry, 1972, p.19-24.

Potable quality hot water at the rate of about 350 gpm is required at the Rochester, N. Y., Gerber Products Plant (baby foods production). The 2 major uses are the empty jar rinsers (where glassware is cleaned and preheated just prior to filling), and the pressure retorts (where about 500 gal/batch of 180° F water is added as a medium in which capped jars are heat processed). Ozonation is used as a method of sterilization in a system that conserves water and steam by recycling.

The water returns to a 20,000 gal holding tank to which make-up city water is added. With an adequate supply of warm water in the storage tank, a 550 gpm pump will transfer on demand to the ozone charge tank. The pump is controlled by a level controller in the charge tank to maintain a water level that will provide a min residence time of 10 min. The ozone charging tank holds 7,500 gal of water and is made of stainless steel to resist corrosion. The tank has a height of 16 ft. Ozone is introduced through ceramic diffusers on the tank bottom. Ozone is produced in a Welsbach Model C-34-D generator.

Water is withdrawn as required from the ozone charging tank by 2 pumps which feed the 2 closed loops.

Major emphasis is placed on the instrumentation which controls the recycled water.

The entire system, including instrumentation, was purchased for about $80,000 in 1968, to which another 30% must be added to include installation ($135,000 total). The savings in water and steam amounts to $125,000/yr, a return on investment of 82%. This results in a payoff period of 1.9 years.

FO-07

Title: "Ozonation of Lactic Acid Fermentation Effluent."

Authors: R.H. Walter & R.M. Sherman

Source: J. Water Poll. Control Fed. 46(7):1800-1803 (1974).

Review: An approach to treating refractory sauerkraut brine not readily treatable in a biological process because of its very high BOD (up to 40,000 mg/l) and high acidity.

Contactor: A gas dispersion cylinder 120 x 24 mm, OD with a medium porosity fritted disc. A small ozonator (Sa[redacted] Co., W. Germany, Type II) was employed, producing 25 mg/hr from oxygen.

Dosages: Very high COD levels (upwards of 15,000 mg/l) were subjected to up to 3 days of ozonation with an influent O_2 flow rate to the ozonator of 9 ml/min. This rate maintained a constant ozone concentration of 400 to 500 mg/l at 25°C.

Results: Lactic acid (I) and sugar (II) were present in filtered or oxygenated brines in concentrations of 1.30 and 0.04 g/ml, resp. After 24 hrs of ozonation, [I] was 0.70 g/ml, and [II] was zero. Pyruvic acid (III) appeared (0.28 g/ml) (but was absent before ozonation), and positive tests for acetaldehyde (IV) and CO_2 were obtained. After 48 hrs of ozonation, [I] was 0.20 g/ml and [III] was 0.03 g/ml. After 72 hrs of ozonation [I] was 0.05 g/ml and [III] was 0.01 g/ml. Thus III is formed upon ozonation, but is destroyed upon further ozonation. IV appears to be an ozonation product of I, II, III, or all 3.

Comment: Efficiency of ozone application was not a concern in this experiment. The ratio of ozone consumed to COD removed in 72 hrs was approximately 2.0. Costs were not projected, but the authors conclude that where ozone generators already have been installed in the food processing industry, and where small batches of refractory effluents are not amenable to biological stabilization, ozonation may be applied as a chemical alternative.

References: 10

FO-08

Title: "Efficiency of Oxygen Demand Reduction of Sauerkraut Brine by Ozone".

Authors: R.H. Walter & R.M. Sherman

Source: *Proc. Second Intl. Symposium on Ozone Technology*, R.G. Rice, P. Pichet & M.-A. Vincent, Editors, Intl. Ozone Assoc., Cleveland, Ohio, 1976, p. 694-704.

Review: Ozone reduced the [COD] of sauerkraut brine in which lactic acid was the major oxidizable constituent. The stoichiometry of the lactate-ozone reaction required a weight ratio of 1.87, or 1.01 in terms of COD. The ratio decreased proportionally with COD during ozonation.

Process: An open loop ozonation system was constructed from a 100 x 8 cm pyrex cylinder to which was fused a fritted glass filter funnel of medium porosity and a stopcock 4 cm above the fritted disc. The stem of the funnel was tapered and connected to an elevated W.R. Grace & Co. Model LG-2-L1 ozonator with 0.25-inch stainless steel tubing. Cylinder oxygen was supplied through a 2-stage diaphragm regulator preset at 10 psi. Flow rate (75 ml/min) was controlled by a stainless steel micrometer needle valve, in-line between the ozonator and the contacting cylinder, and monitored with a soap-film meter at the discharge end of the KI trap.

Results: Lactic acid in water solution was analyzed (0.50 g/l and 90 g/l) and it was found that COD = 0.54 (C) [where C = wt/vol concentration of lactic acid]. Therefore, the theoretical (COD) efficiency index was 0.54 x (1.87) or 1.01. There is a tabular illustration of the ratio of COD removal to ozone generated at 24 hr intervals in 3 liters of brine, which shows the process achieved the greatest efficiency throughout ozonation at the higher concentration. In dilute brine ozone was progressively lost in inverse proportion to the decreased rate of loss of COD.

Conclusion: Existing water quality criteria should be met by dilution after, rather than before, ozonation of sauerkraut brine when effecting COD removal.

Economics: Not discussed.

BR-02

Title: "The Application of Ozone in the Brewery."

Author: E. Du Jardin

Source: Ann. Brass. et Dist., 23:122 (1924). Abstracted in J. Inst. Brewing, London (1925), p. 88.

Review: The germicidal properties of ozone are reinforced and its property of not leaving unwanted by-products upon degradation is mentioned.

The use of ozone for sterilizing aqueous solutions is cited, but its capability to sterilize an environment's atmosphere when added in the air circulation system is questioned. Ozone's ability to deodorize the air is recognized and since it is such a powerful deodorizer, a lesser circulation of air is necessary for removing bad odors. Consequently, the temperature in cellars, etc., is more readily and economically controlled.

BR-03

Title: "Ozone Treatment of Waste Effluent"

Authors: R.R. Furgason, H.L. Harding & M.A. Smith

Source: Research Technical Completion Report, OWRR Project No. A-037-1 DA, Water Resources Research Inst., Univ. of Idaho, April 1973. NTIS Rept. No. PB 220,008.

Review: Describes a portable ozone test unit assembled by the Water Resources Research Inst. at the Univ. of Idaho, and several field tests made with the unit. Details of the portable test unit are as follows:

Reactor Volume	2 gal
Reactor Residence time	1 to 20 min
Feed Rate	0 to 1.5 gpm
Ozone Production	12 g/hr
Contactor	Venturi type

Experimental: The unit was light and easily moved in a van or pickup truck and required only 110 v of electricity, cooling water and the material to be treated for its operation.

This portable ozone test unit was shipped to a major brewery to examine the use of ozone for elimination of tastes and odors. As a result of these tests, the brewer is installing a full-sized plant to treat a portion of the brewery water.

Conclusions: The portable ozone unit has demonstrated its ability to obtain information, but a larger ozonator should be incorporated into the unit; other methods of contacting, however, also should be considered.

Economics: Preliminary estimates indicated costs to be 30¢/1,000 gal for decolorization and deodorization with a full sized plant (size not specified), but the authors recommend further tests on larger scale to refine these estimates.

BR-04

Title: "Concentrated Wort Processing Method".

Author: C.C. Geminn

Source: Master Brewers Assoc. of America, Tech. Quarterly 11(1):21-25 (1974).

Review: Discusses processing of concentrated wort or "high gravity" brews and describes processing at the Genesee Brewing Co., Rochester, N.Y. Dilution water is tap water treated by filtration (through sand and gravel, then activated carbon), ozonation, deaeration, carbonation, cooling and storage.

Dilution Water Treatment: Dilution water should be of the same high quality as the beer, biologically stable, free of odor, taste and oxygen, carbonated and be at the proper pH and temperature. After filtration through sand/gravel, then activated carbon, municipal water (63 gal/min) is ozonized (2 mg/l dosage; 3 to 5 min contact time through diffusers) to polish the water beyond activated carbon filtration to sterilize, remove tastes and odors and possible entrained bacteria. The 0.2 mg/l residual ozone decays in about 6 min.

Deaeration occurs in a separate vessel by spraying heated (to 105°F) ozonized water against the chamber walls under vacuum (28 in of Hg) in the 1st stage. In the 2nd stage, the water is passed through a packed column (ceramic or stainless steel packing). This reduces the oxygen content to 0.15 to 0.20 mg/l. Water then is carbonated to 1.5 to 2.0 vol% CO_2, then cooled to 34° to 36°F and stored at 28 in of Hg in tanks equipped with ceramic diffusers through which a constant low flow of CO_2 is maintained. Blending of this dilution water with concentrated wort is accomplished with an Analog Ratio Blending System, and the beer production process is continued.

Ozone Generator: is not identified, but the subsystem includes an inlet air filter, motor compressor set, dual desiccant tower, 3 dielectric assemblies and variable voltage transformers which range up to 20,000 v. The unit produces 1.5 lbs of ozone/24 hrs or 28.5 g/hr. Clean dry air at 3 to 5 psig and 1.5 cfm is fed through the dielectrics, producing 1% ozone in air.

This unit treats 63 gpm of dilution water with 2 mg/l (by vol) ozone dosages. A dissolved ozone residual of 0.2 mg/l is attained which decays in about 6 min. Power requirements are "the same as burning a 200 watt light bulb, plus an additional cost of about 15 gal/hr of tap water to cool the electrodes".

Contacting: is effected through porous diffusers. Off-gases containing excess ozone are vented to the atmosphere. Ozone concentrations in water are measured by the o-tolidine color comparator test. Residual Cl_2 interferes with this test, but with proper pretreatment (activated carbon) Cl_2 is removed. Biological counts on dilution water consistently plate out zero growth.

BR-05

Title: "Use of Ozonized Water in Yeast Manufacture."

Author: K.G. Mayrhofer & H. Steinhart

Source: Brauwelt 857-859 (1955). Abstracted in J. Inst. Brewing, London 61:530x (1955).

Review: Discusses the water treatment process using ozone, and its incorporation into the yeast manufacturing process. In addition, coverage is given to the biological examination of water, yeast reaction to ozone and behavior of yeast after ozonation.

Bacteria and coliform counts were substantially reduced (to zero) over untreated and filtered water and no apparent effect of the yeast's fermentation abilities were observed, even though its color was affected.

Overall, ozone had no injurious effect on yeast and stabilization was better than in the previous yr when the water had not been treated with ozone. Baking properties and appearance of the yeast also were favorably affected by ozone treatment, and the process imposed no additional technical burden.

BR-06

Title: "Ozonized Water in the Brewing and Mineral Water Industries."

Authors: R. Schäuble & M. Gillardin

Source: Brauerei, Wissenschaft Beil. 11:75-86 (1958). Abstracted in J. Inst. Brewing (London) 64:515 (1958).

Ozonation: Describes progress made in developing plant and equipment for efficient ozonation of water.

Determination of Ozone: Although this material is now historical in nature, the author comments on potentiometric titration, colorimetric methods and acid o-tolidine with NaI.

Germicidal Effects: Experiments were conducted with various forms of yeasts, rhodotorulae, cocci, short rods, mold hyphae and spores to destroy their presence. 0.5 g of ozone/cu m was sufficient to sterilize the water and reduce foreign taste and odor problems. One disadvantage was the waste of ozone caused by the inefficiencies of the mechanical contacting system.

Applications: The author believes ozonation to be excellently suited to the fruit juice industry, and feels its many advantages outweigh the slightly greater cost compared with a chlorination system.

BR-07

Title: "Ozone Generation and Use in the Brewery."

Author: R. I. Tenney

Source: Brewer's Digest 48(6):64-66 (1973).

Review: Discusses ozone production and handling methods. Mention is made of power costs and materials of construction resistant to ozone. Emphasis is placed on small quantity production, in the neighborhood of 10 g/hr. Ozone absorption and toxicity are briefly considered.

Ozone Generator: The basic design for a commercial type corona discharge ozone generator is presented. Oxidation of phenolic wastes from algae growth on tannins to CO_2 and water was accomplished.

Economics: Under ordinary brewery conditions, ozone half-life is approximately 3 min. Power requirements vary from 13 watt hrs/g of ozone to 20 wh/g. Assuming electrical costs to be 1.5¢/kwh, ozone generation costs <30¢/kg. Generating costs are close to 75% of the total operating cost.

10 cfm of clean dried air at 100 psi would suffice to feed small generators with a capacity of 5 to 10 g of ozone production/hr. Generator costs would range from $2,000 to $3,000.

Toxicity: Ozone is toxic to most persons above 100 ppm, when breathed for an hr or more. It may be lethal over the same period at 1,000 ppm. Irritation is experienced at 1 ppm within 10 min of exposure. Odor recognition is impaired by 1 hr exposure to 2.4 ppm of ozone. Adequate control of ozone levels may, under certain circumstances, be accomplished by a simple vent to the outside atmosphere, especially if a number of small production units are employed.

References: 7

BR-08

Title: "Ozone, The Add-Nothing Sterilant"

Author: R.I. Tenney

Source: MBAA Technical Quarterly 10(1):35-41 (1973).

Discusses the physical and chemical properties, production methods, natural occurrence, and sterilizing efficiency of ozone. Applications are presented for water and air purification in breweries. The author is a consultant whose principal interest is applying ozone to the brewing industry. The following is a recommended list of uses of ozone for this industry:

1. Yeast washing with freshly ozonated water containing 1 to 3 ppm of ozone. This will quickly destroy the most easily oxidizable substances in the yeast mass, including melanoidins which create color in the beer residue. Bacteria will be destroyed with minimum damage to the yeast. Use of ozonated water is preferable to bubbling ozonated air directly.

2. Final rinsing of bottles or cans with ozone-containing water will remove trace materials and eliminate beer spoiling microorganisms. The maximum amount of oxygen which will be introduced to the beer is 9 millionths of a gram/bottle, which will have negligible influence on the normal variation in air content.

3. Beer fillers and process equipment such as filters are frequently sterilized before use by circulating hot solutions through them. The cooling water which follows should be sterile. Water containing 1 mg/l ozone would be effective for this use while minimizing the corrosive effect upon brass fittings. If the equipment exposes only impervious surfaces, then a 2 or 3 mg/l ozone solution could be used cold for a sterilant.

4. Rinsing of tanks and pipelines with water containing 1 or 2 mg/l of ozone would be advantageous. This practice is not recommended for rubber hose lines.

5. A final rinse of filter mass with ozonated water just before packing the new pads will insure sterility at this point for those plants still using this equipment. It would be practical to coat the interior of the cake press with polyvinyl chloride or other ozone resistant material. The original bronze would corrode.

6. Brewers have applied ozone for air purification in rooms used by taste panels for controlling mold growth and odors in cellars. Ozone can be used for purifying air in yeast handling areas, in wort cooling and aeration, and might replace chemical scrubbing of CO_2, such as by permanganate.

7. Pretreatment of wastewaters before discharge.

To add 1 mg/l of ozone to a water stream flowing at 1 bbl/min requires 117 mg/min or about 7 g/hr. Unless ozone is needed in the air to reach walls and surfaces, it is generally more efficient to wash the air with ozonated water. Free ozone in the air will discolor brass and bronze fittings, unless they have been Cr plated.

References: 10

BR-09

Title: "The Use of Ozone in Brewing."

Author: M. Van Laer

Source: Petit J. Brass. 36:854-56, (1928). Abstracted in J. Inst. Brewing (London) p. 497 (1928).

Ozone's use in sterilizing brewing water is economical since it requires no after-treatment in the absence of degradation produsts. 2.25 g of ozone is required to sterilize 1 cu m of water. Due to ozone's affinity for degrading organic matter, as much organic matter as possible should be removed in a preliminary wash to ensure its disinfectant properties.

Sterilization of vats, piping, etc. has been more successful with aqueous solutions of ozone as opposed to ozonized air. However, ozonized air has been used to sterilize bottles that have been prewashed.

The author also notes the deodorizing property of ozone and its applications in fermentation rooms.

TYPING GUIDE SHEET

LITERATURE CITED (HOSPITAL WASTEWATERS) (HE)

HE-01 Bryce, C.A., J.A. Heist, R. Leon, R.J. Daley & R.D. Holyer Black, 1973, "MUST Waste Water Treatment System", Final Report to U.S. Army Medical Research & Development Command, Contract DADA 17-71-C-1090.

HE-02 Chian, E.S.K. & P.P.K. Kuo, 1975, "Fundamental Study on the Post Treatment of RO Permeates From Army Wastewaters", First Annual Summary Rept., U.S. Army Medical R & D Command, Washington, D.C., Contract No. DAMD 17-75-C-5006. UILU-ENG-75-2026. NTIS Rept. No. AD-AD-A021 476/7WP.

HE-03* Chian, E.S.K. & P.P.K. Kuo, 1976, "Fundamental Study on the Post Treatment of RO Permeates from Army Wastewater", Sec. Annual Summary Rept. U.S. Army Med. R & D Command, Washington, D.C. Contract DAMD 17-75-C-5006. Rept. No. UILU-ENG 76-2019. NTIS No. AD-A035, 912/5WP.

HE-04 Chian, E.S.K., P.P.K Kuo & B.J. Chang, 1978, "Fundamental Study on the Post Treatment of RO Permeates from Army Wastewaters," U.S. Army Medical Research & Development Command, Ft. Detrick, Md., Contract DAMD 17-75-C-5006, Final Report, 1974-1977.

HE-05 Cowen, W.F., W.J. Cooper & J.W. Highfill, 1975, "Evacuated Gas Sampling Value for Quantitative Head Space Analysis of Volatile Organic Compounds in Water by Gas Chromatography," Analytical Chemistry 47(14):2483.

HE-06 Cowen, W.F. & W.J. Cooper, 1975, "Analysis of Volatile Organic Compounds in Walden Research MUST Integrated Test Samples and in a Laboratory Waste Reverse Osmosis Permeate," Memorandum For Record, Environmental Protection Research Division, U.S. Army Bioengineering Research & Development Laboratory, Ft. Detrick, Md.

HE-07 Gollan, A.Z., K.J. McNulty, R.L. Goldsmith, M.H. Kleper & D.C. Grant, 1976, "Evaluation of Membrane Separation Processes, Carbon Adsorption and Ozonation for Treatment of MUST Hospital Wastes", Final Report to U.S. Army Medical Research and Development Command, Contract DAMD 17-74-C-4066.

HE-08 Hewes, C.G., H.W. Prengle, C.E. Mauk & O.D. Sparkman, 1974, "Oxidation of Refractory Organic Materials by Ozone and UV Light", Final Report to U.S. Army Mobility Equipment Research & Development Center, Ft. Belvoir, Va. Contract DAAK 02-74-C-0239.

HE-09 Hill, A.G. & J.B. Howell, 1977, "Compression of O_3/O_2 and O_3/Air Mixtures", presented at Symp. on Advanced Ozone Technol., Toronto, Ontario, Canada, Nov. Intl. Ozone Assoc., Cleveland, Ohio.

HE-10 Hill, A.G. & J.B. Howell, 1978, "Feasibility of Treating MUST Reverse Osmosis Permeates by High Pressure Ozonation", Final Report to U.S. Army Medical Bioengineering R&D Command, Ft. Detrick, Md., Contract DAMD 17-77-C-7030.

HE-11 Lambert, W.P. & L.H. Reuter, 1976, "Wastewater Reuse Within An Army Field Hospital", Proc. Third Natl. Conf. on Complete Water Reuse, Cincinnati, Ohio. Am. Inst. Chem. Engrs., New York, N.Y.

HE-12 Lambert, W.P. & J.J. McCarthy, 1977, "Ozone Oxidation for Reuse of Army Field Hospital Wastewaters", in Forum on Ozone Disinfection, E.G. Fochtman, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 108-124.

HE-13 Lee, M. & G. See, 1977, "Ozone Technology Presentation", Life Systems, Inc., Engineering Report 314-35, Cleveland, Ohio.

HE-14 Lee, M.K., G.G. See & R.A. Wynveen, 1977, "Reaction Kinetics of UV-Ozone with Organic Compounds in Hospital Wastewater", presented at Symp. on Advanced Ozone Technol., Toronto, Ontario, Canada, Nov. Intl. Ozone Assoc., Cleveland, Ohio.

HE-15 McCarthy, J.J., W.F. Cowen, E.S.K. Chian & B.W. Peterman, 1977, "Evaluation of an Air Stripping-Ozone Contactor System", Technical Report 7707, U.S. Army Medical Bioengineering R&D Laboratory, Ft. Detrick, Md.

HE-16 McCarthy, J.J., W.P. Lambert & L.H. Reuter, 1977, "Research and Development Efforts Concerning Ozonation of Army Field Hospital Wastewaters", presented at Seminar on the Current Status of Ozonation for Wastewater Treatment and Disinfection, Cincinnati, Ohio, Sept. 15. Intl. Ozone Assoc., Cleveland, Ohio.

HE-17 Mix, T.W. & H. Scharen, 1974, "Organic Solute Detection", NTIS Rept. No. PS-770,749, U.S. Dept. of Commerce, 8 p.

HE-18 Mix, T.W. & H. Scharen, 1975, "Development of Techniques for Detection of Low Molecular Weight Contaminants in Product Water from Water Purification of Water Reuse Systems", Final Report to U.S. Army Medical R&D Command, Washington, D.C., Contract DADA 17-72-C-2169.

HE-19 Reuter, L.H., 1975, "Ozone Research Supported by the U.S. Army Medical Research and Development Command," in Proc. First Intl. Symposium on Ozone for Water and Wastewater Treatment, R.G. Rice & M.E. Browning, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 476-482.

HE-20 See, G.G., K.K. Kacholia & R.A. Wynveen, 1975, "Control and Monitor Instrumentation for MUST Water Processing Element", Final Report to U.S. Army Medical R&D Command, Washington, D.C., Contract No. DADA 17-73-C-3163.

HE-21 See, G.G., P.Y. Yang & K.K. Kacholia, 1976, "Research and Development of an Ozone Contactor System", Final Report to U.S. Army Medical Bioengineering R&D Command, Ft. Detrick, Md., Contract DAMD 17-76-C-6041.

HE-22* Sierka, R.A., 1975, "Activated Carbon Treatment and Ozonation of MUST Hospital Composite and Individual Component Waste-waters", Technical Report 7502, U.S. Army Medical Bioengineering R&D Laboratory, Ft. Detrick, Md.

HE-23 Sierka, R.A., 1976, "Mass Transfer and Reaction Rate Studies of Ozonated MUST Wastewaters in the Presence of Sound Waves", Final Report to U.S. Army Medical Research and Development Command, Contract DAMD 17-76-C-6057.

HE-24 Sierka, R.A., 1977, "The Effects of Sonic and Ultrasonic Waves on the Mass Transfer of Ozone and the Oxidation of Organic Substances in Aqueous Solution", Presented at Third Intl. Symp. on Ozone Technol., Paris, France, May, 1977. Intl. Ozone Assoc., Cleveland, Ohio.

HE-25 Sierka, R.A. & R.L. Skaggs, 1978, "Effects of Ultrasound on MUST Hospital Composite Wastewater", Final Report to U.S. Army Medical Bioengineering R&D Command, Ft. Detrick, Md. Contract DAMD 17-77-C-7031.

HE-26* Tencza, S.J. & R.A. Sierka, 1975, "Ozonation of Low Molecular Weight Compounds", Presented at Sec. Natl. Conf. on Water Reuse, May 4-8. Am. Inst. Chem. Engrs., New York, N.Y.

HE-27 Vlahakis, J.G., 1975, "Renovation of a Hospital-Type Wastewater for Recycle", Presented at the Second National Conference on Complete WateReuse, Waters Interface With Energy, Air, and Solids, May. Am. Inst. Chem. Engrs., New York, N.Y.

HE-28* Zeff, J.R., R.R. Barton, B. Smiley & E. Alhadeff, 1974, "UV-Ozone Water Oxidation/Sterilization Process". Final Report #1401 to U.S. Army Medical R&D Command, Contract DADA 17-73C-3138.

HE-29 Zeff, J.D., R. Shuman & E.S. Alhadeff, 1975, "UV-Ozone Water Oxidation/Sterilization Process", Annual Report, U.S. Army Medical R&D Command, Washington, D.C., Contract DAMD 17-75-C-5013.

HE-30 Zeff, J.D., R. Shuman, E.S. Alhadeff, J. Wark, F.C. Farrell, D.T. Boylan & A. Forsythe, 1976, "UV-Ozone Water Oxidation/Sterilization Process", Final Report (;973-1976) to U.S. Army Medical Bioengineering R&D Command, Ft. Detrick, Md., Contract DAMD 17-75-C-5013.

HE-03

Title: "Fundamental Study on the Post-Treatment of RO Permeates from Army Wastewater"

Author: E.S.K. Chian & P.P.K. Kuo

Reference: Sec. Annual Summary Rept., U.S. Army Medical R&D Command, Washington, D.C., Rept. No. UILU-ENG-76-2019, Oct. 1976. Contract No. DAMD 17-75-C-5006.

Nine model organic compounds in aqueous solution were treated with ozone and ozone/UV combinations. The organic compounds studied were: 1-propanol (I), propionic acid (II), 2-propanol (III), methyl ethyl ketone (MEK), acetic acid (HOAC), diethyl ether (IV), o-toluidine (V), methanol (MeOH) and N,N-diethyl-m-toluamide (VI). These compounds were selected because they have been identified in the RO permeates of hospital waste composites.

Ozone was produced from oxygen at 33 mg/l at a gas flow rate of 1 l/min. The contactor was a 4 l fermentor with a stirrer speed of 695 RPM and a 15 watt, low pressure Hg germicidal lamp emitting major UV energy at 253.7 nm. The pH was controlled by means of a solonoid valve which activated HCl or NaOH solns if the pH rose or dropped, respectively, during reaction.

An aqueous solution of I (408 mg/l) was ozonized 1 hr at pH 9. Dissolved ozone concentration was zero, indicating that the ozone demand had not been fully satisfied. Propionaldehyde (VII)(85 mg/l) was formed and a C-balance showed that this and I (145 mg/l remaining) were the only 2 organics present. Starting TOC (225 mg/l) was reduced to 210 mg/l.

UV/ozone treatment of 410 mg/l I under the same conditions produced 95 mg/l of VII; 120 mg/l of I remained after 1 hr, and TOC was reduced to 205 mg/l. In both cases, TOC levels did not start to fall significantly until after the VII formation had peaked (45 min with ozone, 40 min with ozone/UV). This suggests that reduction of TOC concentration occurs by air stripping of VII.

II (490 mg/l) was ozonized at pH 9, at 25°C, over 2 hrs. Dissolved ozone was absent from all solutions, again indicating that the ozone demand had not been satisfied. After 2 hrs the concentration of II was 235 mg/l. TOC concentration dropped from 235 to 200 mg/l. Since not all C was accounted for by the amount of II present, there must have been oxidation products formed which were not detected by gas chromatography. UV/ozonation of II (490 mg/l) under the same conditions lowered its concentration to 60 mg/l in 2 hrs. TOC values fell from 235 to 140 mg/l.

For the balance of this work, lower concentrations of organics were treated, such that concentrations of dissolved ozone of 4 mg/l or higher were determined. Ozonation of II at pH 7 and 25°C removed 17% TOC and gave complete oxidation to acetone. No monocarboxylic acids were detected and acetone accounted for over 85% of the TOC of the reaction mixture.

UV/ozonation of III substantially improved the rate of TOC removal. An initial TOC of 110 mg/l was reduced to 20 mg/l (85%) after 135 min of UV/ozonation. II disappeared after 30 min, at which time the concentration of acetone reached its maximum value; this in turn decreased to zero after 75 min. C_2-C_6 monocarboxylic acids were not detected in the ozonate, but NaOH was required to maintain constant pH. This indicates that formic and/or oxalic acids were produced from oxidation of acetone.

Ozonation of MEK 2 hrs at pH 7 and 25°C produced a small amount of acetate anion. MEK accounted for over 85% of the TOC in the ozonate, and much of the "loss" of MEK was attributed to air stripping (40% of TOC removed after 2 hrs of ozonation). By contrast, after 105 min of UV/ozonation, the concentration of MEK was depleted completely. Acetate ion concentration reached its maximum value after 35 min, then also decreased to zero at 105 min. Trace amounts of acetone and EtOH also were detected.

Ozonation of HOAc 2 hrs at pH 7 (adjusted at beginning, but allowed to rise gradually during treatment) and 25° resulted in 14% removal of TOC. The concentration of glyoxylate anion increased with time, but its concentration was always very low.

UV/ozonation of acetate anion was much more rapid. After 75 min, no acetate was detected. Glyoxylate (at lower concentrations than with ozone alone) remained fairly constant during the first hr, but then disappeared. No alcohols or monocarboxylic acids (other than acetate) were detected. Thus the discrepancy between observed and calculated TOC could only be attributed to the presence of formate and/or oxalate anions. It was proven later that oxalate is present and formate is absent.

Ozonation of IV 2 hrs at pH 9 and 25°C produced ethyl acetate (EtOAc) and acetate anion as the major degradation products, but small amounts of AcH, Me formate, EtOH, acetone and Et formate also were isolated. An overall TOC removal rate of 61% was obtained in 2 stages. Slower removal of TOC occurred during the later stages of ozonation, when EtOAc and acetate anion were the major portions of the TOC. The faster removal rate observed in the earlier stages may have been due to air stripping of IV and its smaller oxidation products (AcH, EtOH, acetone, etc.). Good agreement between the calculated and experimentally determined TOC values indicates that all the oxidation products were accounted for (therefore CO_2 was not an oxidation product).

UV/ozonation gave 94% removal of TOC under the same conditions, because of further oxidation of EtOAc and acetate ion to CO_2. Formation of acetate occurs by 2 routes: 1 from IV, 1 from EtOAc. Small amounts of the same other organics as obtained during ozonation also were isolated after UV/ozonation. Quantitative determination of oxalate and glyoxylate showed that acetate concentration reached zero when oxalate concentration reached its maximum. This indicates that the degradation route of acetate by UV/ozonation is through glyoxylate and oxalate to CO_2. Since the amount of oxalate formed was not equal to the amount of acetate present, it is likely that glyoxylate (precursor of oxalate) can be oxidized directly to CO_2.

Ozonation of V 2 hrs at pH 9 and 25°C produced 42% TOC removal, but no V was observed after 15 min. Acetate (about 10 ppm as C) was identified and its concentration decreased only gradually with time. Oxalate concentration was slightly higher than that of acetate and appeared to be resistant to ozonation. Glyoxylate also was identified.

UV/ozonation of V showed 2 different zero order TOC removal rates. During the first 15 min, all V disappeared completely. Acetate and oxalate formed during the initial stages, but neither substance was present after 75 min of reaction. Cleavage of the benzene ring appears to be the major mechanism by which V disappears, and no aromatic compounds were detected either by gas chromatography or by UV absorption at 210 to 270 nm. Volatile aldehydes, ketones, esters and acids also were not detected, thus the unaccounted for organics likely are aliphatic amino compds. Final nitrate-N accounted for 34 and 40% of the initial N present (in ozonation and UV/ozonation, respectively), and the remainder probably was present as organic-N and/or stripped-off NH_3.

Ozonation of MeOH 2 hrs at pH 9 and 25°C produced HCHO and HCOOH as the only 2 oxidation products. Organic removal was only 72% after 2 hrs, and its rate slowed after 75 min. UV/ozonation of MeOH gave the same results.

Ozonation of VI 2 hrs at pH 9 and 25° showed no VI or other aromatic compounds after 15 min. Formic, acetic and oxalic acids were isolated, and their concentrations were at maximum values after 2 hrs. TOC level was reduced from 85 to 45 mg/l. Oxalate concentration was 20 mg/l after 2 hrs of ozonation.

UV/ozonation gave similar results but acetic and oxalic acids were further oxidized toward the end of the period, and their concentrations decreased. HCOOH concentration passed through a minimum, thus it is produced from more than 1 source. TOC levels decreased from 82 to 28 mg/l. All organic carbon was accounted for after 105 min. 45% of VI-N had been oxidized to nitrate after 2 hrs, the unaccounted for N probably having been stripped off as ammonia. The same result (46% of VI-N found as nitrate) was obtained by ozonation alone, but 12.5% of the TOC could not be accounted for after 2 hrs. Thus the balance of the N could have been stripped NH_3, but also organic-N (aliphatic amines).

Summary: Oxidation of formic, glyoxylic and oxalic acids (major end products of all 9 compounds, along with acetic acid) to CO_2 is believed to be the major mechanism of organic removal by ozonation. HOAc oxidizes to glyoxylic acid which further oxidizes to oxalic acid or to CO_2 (or both). Ozonation of glyoxylic acid is rapid, since large amounts of it never were found. AcH, EtOH, EtOAc, IV, and MEK all produced HOAc. HCOOH forms by oxidation of large molecules as well as from HCHO and MeOH. Cleavage of the aromatic ring is very rapid, even without UV. UV enhanced the rates of initial oxidation of all compounds studied except MeOH and IV, but did enhance the oxidation rates of their initial oxidation products.

HE-22

Title: "Activated Carbon Treatment and Ozonation of MUST Hospital and Individual Component Wastewaters"

Author: R.A. Sierka

Source: Tech. Report 7502, U.S. Army Medical Bioengineering R&D Laboratory, Ft. Detrick, Md. (1975)

Review: The objective of this work was to identify the capabilities of activated carbon and ozone to reduce the TOC and COD levels of the MUST laundry composite waste, the MUST hospital composite waste, as well as of their individual component streams, to 10 and 5 mg/l levels, resp. The component streams consisted of shower, operating room, kitchen, lab and X-ray lab wastes and have the following characteristics:

Parameter	hospital composite wastewater	laundry composite wastewater
TDS (mg/l)	1,240	1,630
SS (mg/l)	70	194
pH	6.6	10.5
COD (mg/l)	870	1,740
TOC (mg/l)	229	457

The activated carbon and ozone treatments were studied as post-treatments after ultrafiltration (UF) and reverse osmosis (RO). Adsorption isotherms were determined on the UF and RO treated wastes at ambient conditions of pH and temperature and at pH 7.0. The solutions then were filtered and analyzed for TOC, inorganic carbon, total carbon and foaming potential.

Treated wastes were ozonized at ambient conditions, then post-treated with activated carbon filtration, then analyzed for TOC, total carbon and inorganic carbon. Tests also were made skipping the activated carbon step. Ozonation was effective in reducing the shower wastes levels to the 5 mg/l TOC objective, but only after 120 min of treatment. For RO permeates, ozonation for 60 min is required. Lab wastewaters were the least responsive to treatment.

Carbon Adsorption Isotherm Tests -- These were performed by contacting 250 ml of water with known weights of powdered activated carbon (PAC) (Filtrasorb-400) for 2 hrs at room temperature (24°), then filtering through a 0.45 μ Millipore membrane. 60 ml of filtrate was used for TOC analysis and the foaming potential test.

Foaming Potential Test (FPT) -- was conducted by placing 50 ml of sample in a 250 ml graduated cylinder and sparging with ozone for 15 sec. The height and properties of the foam at cessation of ozonation were recorded.

Ozonation Tests -- An ozone reactor was constructed from a 4 liter Nalgene plastic graduated cylinder cut off at the 3,500 ml mark, a 1/18 hp motor at 350 RPM and containing 2 lucite baffles extending 0.5 inch into the cylinder at 180° to each other running from the top to bottom of the cylinder.

Ozone was generated in a W.R. Grace Model LG-2-L1 corona generator at a rate of 167 mg/min. The reactor was filled with wastewater to the 2 liter mark, a small aliquot was removed for an initial TOC analysis. The UV spectrophotometric method of Shechter was used to monitor ambient aqueous concentrations of ozone.

UF permeates were treated with 1,000 mg/l of PAC prior to ozonation and mixed at 150 RPM for 1/2 hr using a 1/18 hp motor with a 2-bladed propeller.

Economics: No figures were given, although the U.S. Army is evaluating this system to identify possible processing trade-offs to meet Army requirements with respect to power, weight, cost, ease of maintenance, reliability, safety, and simplicity of operation.

References: 7

HE-26

Title: "Ozonation of Low Molecular Weight Compounds"

Authors: S.J. Tencza and R.A. Sierka

Source: Presented at Sec. Natl. Conf. on Water Reuse, May 4-8 (1975). Am. Inst. Chem. Engrs., New York, N.Y.

Review: Ozonation of aqueous solutions of formic, acetic, propionic and butyric acids, butyl and isobutyl alcohols, butyraldehyde and methyl ethyl ketone was studied. These materials are not rejected well by reverse osmosis membranes. In addition, oxidant concentrations, mixing temperature and pH were investigated for their effects on the oxidation rates.

Contactor: Ozone was generated in oxygen and passed through a 12 in high, 3.5 in diameter sparger reactor containing 2 opposite baffles which eliminated a mixing vortex. Sample size was 1.2 l for all experiments, and changes in COD were measured.

At a mixing speed of 1500 RPM the interfacial area for transfer of ozone gas approached its maximum value, and this was the speed used for all experiments. Ozone production rate was 8,210 mg/hr.

Butyric acid was the easiest butyl compound to oxidize by ozone, followed by the alcohols, methyl ethyl ketone and butyraldehyde. Formic acid was the easiest to oxidize to CO_2 and water---99% was converted in 15 min. Ease of oxidation decreased in the order: formic, butyric, acetic, then propionic acids. The most influential parameters were pH, temperature, mixing and ozone concentration, in that order.

References: 28

HE-30

Title: "UV-Ozone Water Oxidation/Sterilization Process"

Authors: J. Zeff, R. Barton, B. Smiley & E. Alhadeff

Source: Westgate Research Corporation, Final Report #1401, to U.S. Army Medical R&D Command, Washington, D.C. Contract DADA 17-73C-3138, Sept., 1974.

Review: A detailed report of tests performed to determine the feasibility of combining ozonation and UV radiation simultaneously to remove predetermined levels of microbial contaminants and organic substances from water. Stirred reactors and column reactors were compared, with column reactors apparently being more effective; a definition was made of the general constraints for operating variables.

The combination of UV and ozone was more effective in destroying the microbial and organic contaminants. 99.7% of the organisms present were destroyed by about 2.25 mg/l of ozone plus UV; 3 mg/l of ozone plus UV resulted in their complete destruction. 0.07 mg of ozone and 0.1 watt of 253.7 nm UV could reduce the TOC level of tap water from 10 to 2 mg/l in 1 minute. 90% of 10 mg/l hydroquinone and pyrogallol in 3 l batches were removed by 65 mg of ozone in 1 hr. UV plus air without ozone oxidized 80% of 10 mg/l hydroquinone, 75% of 10 mg/l pyrogallol and 40% of 10 mg/l of xylenol in 1 hr. Increasing the temperature to 50° had little effect on reaction rate of the above compounds. The energy demand of the non-optimized process is 8 to 10 watt hours/lb of water processed. Reaction products were not identified.

No chemical changes were detected upon treating acetate ion or urea with UV/ozone. All 3 aromatics were significantly degraded by UV alone in a 60 min period: hydroquinone-39%; pyrogallol-33%; xylenol-28%.

Ozone Generator: The UV light and ozone gas were generated with 1 to 3 4-watt mercury UV ozone lamps installed above the surface of the water in the reactor.

Contact: A 1 gal stirred batch battery jar reactor was used, and column reactors were investigated in comparison. All 3 aromatic compounds were oxidized to a greater extent in 60 min in the column reactor, compared with the batch reactor. The UV lamp extended throughout the length of the column reactor. Power demand of the UV lamp is 50 watts and ozone generation requires 10 watts. Three l, or 6.6 lbs of water can be treated in 1 hr; thus 9.1 watt-hours are required to treat 1 lb of water. This does not include energy required for pumping or compressing. References: 19.

LITERATURE CITED (INORGANICS) (IC)

IC-01* Geisel, R., H. Krause & W. Kluger, 1972, "Decontamination of Radioactive Waters", Ger. Patent 2,120,754, 9 Nov., Addn. to Ger. Patent 1,517,664 (Chem. Abstr. 75:40130x for 1,517,664).

IC-02* Lizunov, V.V., E.V. Leontovich, & V.A. Skripnik, 1972, "Ozone Oxidation of Mercury in Waste Waters from Chlorine and Alkali Production", Vodopodgotovka Ochistka Prom. Stokov 9:19-22 (Russ). From Ref. Zh., Khim, 1972, Abstr. No. 171412.

IC-03 Marcy, J. & F. Matthes, 1967, "The Reaction of Manganese (II) Salt Solution with Ozone", Chem. Tech. 19:430.

IC-04* Netzer, A., A. Bowers & J.D. Norman, 1972, "Removal of Trace Metals from Waste Water by Lime and Ozonation", Pollut. Eng. Sci. Solutions, Proc. Intl. Meet. Soc. Eng. Sci., 1st, (Pub. 1973), p. 380-386.

IC-05 Netzer, A. & A. Bowers, 1975, "Removal of Trace Metals from Wastewater by Lime and Ozonation", in *Proc. First Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 731-747.

IC-06 Rohner, E., 1969, "Removal of Manganese in Water with Ozone", Swiss Patent 481,020, December 31.

IC-07 Senzaki, T. & A. Ikehata, 1968, "Oxidation of Manganese (II) in Aqueous Solutions by Ozone", Kogyo Yosui, 116:46; Chem. Abstr. 69:100209t (1968).

IC-08 Sergeev, 1964, Y.S., "Iron Removal and Quality Improvement of Alluvial Water", Kommun Khoz. sb., 2:72, Chem. Abstr. 65:5218g (1966).

IC-09* Shambaugh, R.L. & P.B. Melnyk, 1978, "Removal of Heavy Metals via Ozonation", J. Water Poll. Control Fed. 50:113.

IC-10 Singer, P.C. & W.B. Zilli, 1975, "Ozonation of Ammonia in Municipal Wastewater", in *Proc. First Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 269-287.

IC-11 Somiya, I., H. Yamada & T. Goda, 1977, "The Ozonation of Nitrogenous Compounds in Water", presented at Symp. on Advanced Ozone Technol., Toronto, Ontario, Canada, Nov. Intl. Ozone Assoc., Cleveland, Ohio.

IC-12* Weber, P. & W.L. Waters, 1973, "Ozonation of Aqueous Dimethylmercury", Proc. Montana Acad. Sci., 32:66-69.

IC-13 Whitson, J.T.B., 1947, "The Effect of Ozone on Waters Containing Manganese", J. Inst. Water Engrs. 1:464.

IC-14 Yakobi, V.A., G.A. Galstyan & T.M. Galstyan, 1975, "Oxidation of Compounds of Trivalent Chromium by Ozone", Zhurnal Prikladnoi Khimii 48(1):16-19.

IC-01

Title: "Decontamination of Radioactive Waters

Authors: R. Giesel, H. Krause & W. Kluger

Source: German Patent 2,120,754, 9 Nov. 1972; Addn to German Patent 1,517,664 (Chem. Abstr. 75:40130x for 1,517,664)

Foaming during evaporation of radioactive wastewater is prevented by ozonation before evaporation.

IC-02

Title: "Ozone Oxidation of Mercury in Waste Waters From Chlorine and Alkali Production"

Authors: V.V. Lizunov, E.V. Leontovich & V.A. Skripnik

Source: Vodopodgotovka Ochistka Prom. Stokov 9:19-22 (1972) (Russ.). From Ref. Zh. Khim., 1972, Abstr. No. 171412

An air mixture with 22 to 24 ppm of ozone was passed through a 50 mm x 2 m column containing 0.124 mg/l of Hg in wastewater for 6 to 32 minutes. The oxidation rate increased with decreasing pH and was complete at pH 4. No metallic Hg vapor was produced.

IC-04

Title: "Removal of Trace Metals From Waste Water by Lime and Ozonation"

Authors: A. Netzer, A. Bowers & J.D. Norman

Source: Pollut. Engr. Sci. Solns., Proc. Intl. Meet. Soc. Engr. Sci., 1st, 1972 (Publ. 1973), p. 380-386

A bench scale plant for removal of trace metals by lime and ozonation is described. Stock solutions of metals were prepared to a concentration of about 100 mg/l; the exact concentrations were determined spectrophotometrically. Lime was added to adjust the pH to 7 to 9. Ozonation was carried out to saturation in a 120 x 6.5 cm perspex column. Metal removal was >99.5% for Al, Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn. Hg removal was lower.

IC-09

Title: "Removal of Heavy Metals by Ozonation"

Authors: R.L. Shambaugh & P.B. Melnyk

Source: J. Water Poll. Control Fed. 50:113 (1978)

Toxic heavy metals are present in many industrial and municipal wastes and potable streams, in both complexed and uncomplexed forms. Ozonation was investigated as a method of removing heavy metals. Reaction rate constants for the 2nd-order reaction of aqueous ozone with EDTA-complexed Mn, Cd, Ni and Pb are 1.39×10^5, 1.52×10^5, 2.88×10^5 and 2.96×10^5 cu cm/mole, resp. The ozonation of uncomplexed Pb, Mn, Ni, Co, Ba and Zn was investigated. When higher oxidation states of the metal ion are possible, the ozone oxidation of uncomplexed metals appears to be very rapid, with reaction rate constants exceeding 10^9 cu cm/mole.

IC-12

Title: "Ozonation of Aqueous Dimethylmercury"

Authors: P. Weber & W.L. Waters

Source: Proc. Montana Acad. Sci. 32:66-69 (1973)

Generator: Welsbach, Model T-408 operating with oxygen at 0.01 mmole/min produced 4% ozone in oxygen.

Contactor: A reaction flask maintained at 25°C.

Experimental: Dimethylmercury (I) solutions in water (0.0005 M) were ozonized about 10 minutes. The reaction was too fast to allow calculation of a rate constant or reaction order. This agrees with earlier work on the same reaction in chloroform. No detectable I remained after 10 minutes of ozonation (limit of detection, 0.00005 M), and at least 90% had reacted.

Expected reaction products (HCOOH, CO_2, HgO) were not identified. It was concluded that ozonation can be used to remove alkylmercurials from water and wastewater.

References: 7.

LITERATURE CITED -- IRON & STEEL (IS)

IS-01 Anonymous, 1951a, "Ozone Kills Phenols in Waste", Chem. Engineering 225-228, Sept. 1951.

IS-02 Anonymous, 1951b, "Phenol Wastes, Treatment by Chemical Oxidation", Cooperative Study, Ohio River Valley Water Sanitation Commission, Cincinnati, Ohio, 15 June 1951.

IS-03 Cleary, E.J. & J.E. Kinney, 1951, "Findings from a Cooperative Study of Phenol Waste Treatment", Engineering Bull., Purdue Univ. Engr. Ext. Serv. 76:158-170.

IS-04* Hall, D.A., 1958, "The Treatment of Coke Works Effluent with Ozone", Gas World 147(3829): Coking Sect. 52(539):7-13.

IS-05* Hall, D.A. & G.R. Nellist, 1959, "Treatment of Phenolic Effluents", J. Appl. Chem. 9:565-576.

IS-06* Hall, D.A. & G.R. Nellist, 1965, "Phenolic Effluents Treatment", Chem. Trade. J. & Chem. Engineer 156(4072):786.

IS-07* Kucharski, J.K., E. Ladouceur & B.P. Le Clair, 1976, "Treatment of Blast Furnace Scrubber Water", Presented at 11th Canadian Symp. on Water Pollution Research, Burlington, Ontario, 5 Feb.

IS-08 Leggett, 1920, U.S. Patent 1,341,913.

IS-09 Marechal, 1905, French Patent 350,679.

IS-10* Murdock, H.R., 1951, "Ozone Provides an Economical Means for Oxidizing Phenolic Compounds in Coke Oven Wastes", Indl. Engr. Chem. 43(11):125A, 126A, 128A.

IS-11 Niegowski, S.J., 1953, "Destruction of Phenols by Oxidation with Ozone", Indl. Engrg. Chem. 45:632.

IS-12* Nebolsine, R., 1957, "The Treatment of Waterborne Wastes from Steel Plants", Iron & Steel Engr., Dec., p. 125-150.

IS-13* Prober, R., P.B. Melnyk & L.A. Mansfield, 1977, "Ozone-Ultraviolet Treatment of Coke Oven and Blast Furnace Effluents for Destruction of Ferricyanides", Presented at 32nd Annual Indl. Waste Conf., Purdue Univ., Lafayette, Indiana, May.

IS-14 Rozhnyatovskii, I.I., D.P. Dubrovaskaya & F.A. Melamed, 1959, "The Purification of Waste Waters from Coke Plants by Ozonation". Koks i Khim, 7:63-66.

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IS-04

Title: "The Treatment of Coke Works Effluent with Ozone"

Author: D.A. Hall

Source: Gas World 147(3829):Coking Sect. 52(539):7-13 (1958)

Review: Laboratory ozonation studies were conducted on iron and steel wastes. Durham coke works ammoniacal waste liquors were ozonized, destroying most normal chemicals present (cyanides, thiocyanates, sulfides, thiosulfates) but leaving a high oxygen absorption value (OAV) and producing other obnoxious substances (cyanides from thiocyanates, oxalic acid and sulfuric acid). About 150 mg/l of final OAV was due to oxalic acid, which, though not detectable before ozonation, was present afterward in amounts up to 800 mg/l. Other OAV apparently was due to some condensation products of a resin or gum type. The liquor became almost colorless after ozonation, after passing through a dark brown or nearly black intermediate stage. The following compounds present in ammoniacal waste liquor were tested:

(1) Phenols. The ozone/phenol ratio averaged 1.7, varying between 0.7 and 2.8 (17 lb of ozone would be required/1,000 gal of ammoniacal waste liquor). The efficiency of ozonation could be increased by about 25% by increasing the pH of the original liquor to about 10.

(2) Polyhydric phenols. These were destroyed by ozonation, though somewhat more slowly than were monohydric compounds. In the ozonation of pure dihydric phenols there was an apparent production of phenol-aldehyde resins, which themselves were ozonized at a later stage in the process.

(3) Thiosulfates. At concentrations up to about 4,000 mg/l complete destruction of the thiosulfate took place in the early stages of ozonation; about 98% of the sulfur was converted to sulfuric acid.

(4) Thiocyanates and Cyanides. Thiocyanates were converted to CN^-, which was oxidized to CNO^- only after phenols had been completely oxidized. CNO^- underwent complete oxidation to CO_2 and N_2. Ammonium sulfate and sulfuric acid also were formed. Increased pH had the reverse effect on CNO^- oxidation as on phenol oxidation, the reaction slowing down considerably at pH >8.0. At an initial pH of 11.5 the time required for destruction of SCN^- was nearly 10 times that at pH <8.0. There was practically no accumulation of CN^- when the pH was >9.0; otherwise the maximum CN^- concentration reached usually varied between 25 and 50 mg/l.

(5) Sulfides. At concentrations up to at least 108 mg/l, sulfides were easily oxidized to sulfuric acid.

(6) Ferrocyanides. Conversion to ferricyanide may have occurred to a small extent, as the liquor sometimes turned a pale blue color.

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Ozonation was a more efficient process when used after pretreatment by froth flotation or by biological means. In the first case, <1 lb of ozone destroyed all the phenols in 1,000 gal of pretreated liquor; when phenol concentrations were reduced to <1 mg/l, the ozone/phenol ratio was about 3:1, there was only a small change in pH, and OAV was reduced to about 20. In the second case, ozonation destroyed phenols and thiocyanates, and reduced the OAV, but an increase in [CN^-] occurred which could be eliminated completely only by doubling the ozone dosage. The efficiency of ozone absorption decreased rapidly after completion of phenol oxidation. The use of ferrous sulfate or chlorine would be more economical for the removal of CN^- created upon ozonation of SCN^-.

Ozone Generation: A Tack Air Conditioning Co., Ltd. "Ozonair" apparatus, produced 2.5 g ozone/hr (12,000 volts) at a concentration of about 5 mg/l and dry air throughput rate of 6 l/ min. Contactor details are not given.

Contact: Ozonized air was distributed by a sintered glass filter upwards through the waste liquor in a vertical wide-bore glass tube. The amount of air required to give an ozone dosage of 200 (or 300) mg/l was passed through at about 25 l/hr. Ozone was measured in the influent and effluent gases, so that the amount of ozone actually consumed was determined.

Economics: Costs were estimated at about 42¢/lb of ozone for a plant producing 10 lb ozone/hr. This was further broken down as follows: 14¢ for depreciation and interest, 14¢ for power, 7¢ for labor, and 7¢ for maintenance and replacements. With 1 ton of coal producing 30 to 70 gal of ammoniacal waste liquor, process costs varied from <14¢/ton of coal to about 49¢/ton, averaging about 28¢/ton of coal carbonized (1958 prices). Although ozonation costs for these Fe and steel wastes are much cheaper than other chemical costs suggested so far, they would still be a very big burden to a coke works. As a finishing process, however, following pretreatment by dephenolization, froth flotation or biological oxidation, about 3 lb of ozone/1,000 of gal waste liquor, 1 to 2 lbs, or 1 lb can be used, resp., (rather than 17 lb/1,000 gal). The final treatment thus would average about 3¢/ton of coal.

Conclusions: Phenols can be easily and completely destroyed by ozone, but it is the side reactions which become of importance in dealing with ammoniacal spent liquor. Thiocyanates are completely and rapidly destroyed in neutral or acid solutions, producing first CN^-, then CNO^-, but the reaction is slower at higher pH. Thiosulfates are easily oxidized. These substances are broken down before oxidation of phenols begins. Moreover, destruction of phenols is more efficient in alkaline solution. Thus pH adjustment could be used to give preferential oxidation of either phenols or thiocyanates.

Thiocyanates are converted to CN^- by ozone, but these now are not fully oxidized until the phenol has disappeared. In addition, sulfuric and oxalic acids are produced, and there is high residual OAV due to unidentified compounds. In alkaline solutions (pH >10), however, the increase in [CN^-] upon ozonation does not occur.

The amount of ozone required to oxidize 1 unit of phenol increases as the total [phenol] is reduced, especially at very low concentrations. At higher [phenol], the ratio is sometimes <1. To reduce [phenol] to <1 mg/l for treated liquors containing 50 mg/l, the ozone/phenol ratio is 3; but when the initial liquor contains only 5 mg/l, the ratio becomes 10:1.

References: 8

IS-05

Title: "Treatment of Phenolic Effluents"

Authors: D.A. Hall & G.R. Nellist

Source: J. Appl. Chem. 9:565-576 (1959)

A review article describing treatment of phenolic effluents iron and steel plants.

Marechal patented the use of ozone for oxidation of phenols in 1905 (French Patent 350,679). In ammoniacal wastewaters, ozone is more effective in removing phenols than chlorine, which must destroy chloramines produced before phenols are attacked. Chlorine dioxide does not react with ammonia, reacts with phenols, but is more costly than ozone.

Laboratory experiments were conducted using an ozone contactor 3 ft high and 3 in diameter. Each batch was 1,500 ml in volume. Ozonized air (5 mg/l) was diffused through a sintered tube. The generator was not specified.

Effluent from a coke oven froth flotation plant required <1 lb/1,000 gal to destroy all phenols (initial concentration about 100 mg/l). The ozone/-phenol ratio for removal of phenol to <1 mg/l was about 3/1, and the cost of ozonizing froth flotation plant effluent would add 2¢ to 5¢/ton of coke to the plant costs (at 42¢/lb of ozone).

In ozonation of raw spent ammoniacal liquors, the ozone/phenol ratio was affected by the non-phenolic components (thiosulfates and thiocyanates), and averaged 1.7 (0.7 to 2.8). Thus on average, 17 lbs of ozone/1,000 gal of ammoniacal liquor were required to reduce an initial phenol content of 100 mg/l to <1 mg/l.

One difficulty in ozonizing ammoniacal liquors is intense frothing during the early stages. This makes the average cost about 35¢/ton of coke produced. While this is much cheaper than other suggested chemical processes for phenols removal, it poses a very large burden on a coke works and is much more expensive than froth flotation followed by ozonation.
Increasing pH to about 10 increases efficiency of ozone utilization about 25%, which would lower ozonation costs by about 25%.

For high phenol-containing effluents, dephenolization (rotary contactor) should be the first step, followed by biological treatment or froth flotation to reduce phenol concentrations to 10 to 50 mg/l. If further reductions are necessary, ozonation now can produce an effluent containing <1 mg/l.

References: 16

IS-06

Title: "Phenolic Effluents Treatment"

Authors: D.A. Hall & G.R. Nellist

Source: Chem. Trade J. & Chem. Engineer, 156(4072):786 (1965)

Reviews ORSANCO (Ohio River Valley Water Sanitation Commission) 1951 study of treatment of phenol-containing (100 mg/l) effluents with ozone, chlorine and chlorine dioxide. All were successful technically, but ozone was the most cost-effective, was free of obnoxiuos residuals and had no interferences from ammonia (Abstractors' Note: Pure chlorine dioxide does not react with ammonia. However, when synthesized using excess chlorine, then the excess chlorine will react with ammonia.) For complete oxidation of phenol, however, 6 parts of ozone were required/part of phenol.

In the present work, 15 different British coke works liquors were tested batchwise with ozone (in 1958). Ozone/phenol ratios ranged from 0.7 to 2.8, with an average of 1.7. Assuming 42¢/lb for the cost of ozone in Britain at the time, the cost of coke oven effluent ozonation was estimated to be $7.14/-1,000 gal, or 40¢/ton of coal carbonized. This cost was judged to be excessive. In addition, thiosulfate and SCN^- are oxidized by ozone to (eventually) sulfuric acid. SCN^- reacts very rapidly with ozone to produce CN^-, which reacts more slowly with ozone.

Bioaeration of ammoniacal spent liquors removed most of the phenols and SCN^-. Thus, ozonation has possibilities as a polishing process after biological treatment of coke oven wastes. Experiments were conducted to determine optimum ozonation conditions and effluent qualities.

Contactor: Liquor and ozonized air (6 mg/l vol) flowed cocurrent through an annular tower. The outer tube was 30 in long and 2.5 in internal diameter; the inner tube was 1.5 in external diameter and 19 in high. Eleven circular plates spaced evenly in the annular space between the 2 tubes were fixed firmly on the inner tube and sloped slightly downward. They were divided into 6 equal sectors by means of slots, 0.1 in wide. The discs were staggered so that the slots in the next lower disc were below the sector blades of the disc above, each disc being rotated through 30°, compared with the adjacent discs above and below.

Conclusions: In a 2-staged process using this type of reactor, it should be possible to produce an effluent containing a residual permanganate value (P.V.) of about 30 mg/l from a coke works spent liquor which has been biologically treated. Ozone consumption should not exceed 1.5 lbs/lb of P.V. destroyed. Assuming that ozone costs 42¢/lb and that the original waste liquor was diluted by 3 times its volume with clean water in the biological treatment plant, the cost of ozonation would be about $1.12/1,000 gal of ammonical spent liquor, or 6¢/ton of coal carbonized.

IS-07

Title: "Treatment of Blast Furnace Scrubber Water"

Authors: J. K. Kucharski, E. Ladouceur & B.P. Le Clair

Source: Presented at 11th Canadian Symp on Water Pollution Research, Burlington, Ontario, 5 Feb. 1976

A bench scale research program is described employing treatment alternatives for 2 modes of operation (once through and recycle with blowdown), and using wastewaters of the Steel Co. of Canada, Ltd. Concentrations of CN^-, phenol, ammonia, heavy metals and their removal were investigated. Ozonation was utilized for destruction of phenols and simple and complex cyanides, and effects of pH, temperature and catalysts were examined.

Total [CN^-] in the untreated, recycled blowdown water did not exceed 1 mg/l, and fluctuated in the water from the once-through system from 10 to 16 mg/l. CN^- removal by ozone was technically and economically feasible. Simple CN^- was easily reduced in concentration to <0.05 mg/l, but similar reductions in total CN^- concentration were possible only in the presence of catalysts [Cu(II) and Mn(IV)].

Phenolic compounds were oxidized by ozone to <0.02 mg/l before CN^- was removed. Reduction in ammonium ion concentration by ozone was feasible, but required raising the pH above 9. Some catalytic effect of heavy metals on reaction rate also was observed. Air-stripping of ammonia is feasible as a 2nd stage, following CN^- and phenol oxidation by ozone. This 2nd stage also removed heavy metals because of the high pH.

Technical and economic considerations were examined for in-plant reuse of the treated recycle blowdown waters (but are not discussed in the abstract).

IS-10

Title: "Ozone Provides an Economical Means for Oxidizing Phenolic Compounds in Coke Oven Wastes"

Author: H.R. Murdock

Source: Indl. Engr. Chem. 43(11):125A, 126A, 128A (1951)

This research project was sponsored by the Ohio River Valley Water Sanitation Commission and several iron and steel companies. Effluent from an ammonia still following a Koppers vapor recirculation dephenolizer was used to obtain laboratory, then pilot plant data. Engineering data necessary for design of a full scale facility also were obtained. Phenol contents from the still effluent varied from 28 to 332 mg/l, and the objective was to reduce this to 5 parts/billion, the taste-producing limit for water supply.

Laboratory studies indicated that ozone, chlorine and chlorine dioxide would destroy phenols. Ozone (400 mg/l) reduced the phenols content of 2 ammonia still wastes containing 170 and 80 mg/l to about 5 mg/l; 500 mg/l of ozone reduced them both to nearly zero. Much less ozone (160 mg/l) was required to reduce 80 mg/l of pure phenol to zero.

6,000 mg/l of chlorine was required to reduce 170 and 80 mg/l of phenols in still wastes to 3 mg/l, probably because chlorine oxidizes ammonia and ozone does not. Thus the cost of treating phenols in an ammonia still waste with ozone is less than the cost of treating with chlorine.

In a 100-oven coke plant, the fixed and operating costs for ozone treatment of phenols are estimated to be 3¢/ton of coal carbonized. Costs for a 300-oven plant are estimated at 2¢/ton of coal carbonized. Using oxygen, the cost would approach 1.25¢/ton of coal, but the oxygen would have to be recycled. These estimates assume 12 yr depreciation of ozonation equipment. With 5 yr amortization, a large plant could expect costs of 1¢/ton of coal carbonized. Corresponding chlorination costs would be 2 to 3 times as high as ozonation costs.

No discussion is given of ClO_2 experiments nor of the ozone contactor. A Welsbach ozone generator, using air feed gas, was used.

IS-12

Title: "The Treatment of Waterborne Wastes from Steel Plants"

Author: R. Nebolsine

Source: Iron & Steel Engineer, 125-151 Dec. 1957

A comprehensive review of wastewater treatment in steel plants written by a consulting engineer, but reports no experimental data nor cites references. Use of ozone is mentioned, along with chlorine and chlorine dioxide, as a chemical oxidant for phenolic wastes only.

Use of chlorine is sensitive to dosage, pH and temperature. If the chlorine dosage falls too low, phenols are not destroyed, but are converted to chlorophenols, which present a worse disposal problem than the original phenols. An excessively large quantity of chlorine is required to reduce phenol concentrations to the low limits desired.

Neither ozone nor chlorine dioxide are as sensitive as chlorine to operating conditions and they do not produce complications if underfed. Ozone requires a large initial investment, but has relatively low operating costs. Chlorine dioxide requires lower investment than ozone, but has higher operating costs.

IS-13

Title: "Ozone-Ultraviolet Treatment of Coke Oven and Blast Furnace Effluents for Destruction of Ferricyanides"

Authors: R. Prober, P.B. Melnyk & L.A. Mansfield

Source: Presented at 32nd Annual Industrial Waste Conference, Purdue University, West Lafayette, Indiana, May 10-14, 1977.

Preliminary results are presented for destruction of ferricyanide in simulated blast furnace effluent and coking liquor compositions.

Decomposition rates of iron-cyanide complexes in the presence of ozone and UV irradiation were determined for pH 4.5 to 9.5, 8° to 50°C, ozone feed rates of 0 to 65 mg/l-min, and UV intensities of 0 to 10 watts/l.

Ozone/UV treatment resulted in effective destruction of ferricyanide. This was attributed to a synergistic effect of the UV irradiation on ozone, which generates highly reactive species.

Ozone consumption was 5 to 80 fold greater than stoichiometric requirements, due to parasitic reactions of ozone.

LITERATURE CITED -- LEATHER TANNERIES (LT)

LT-01 Dye, J.D., 1956, "The Treatment and Disposal of Tannery Wastes", in The Chemistry and Technology of Leather, F. O'Flaherty et al., editors, Reinhold Publ. Corp., New York, N.Y.

LT-02* Eye, J.D. & D.P. Clement, 1972, "Oxidation of Sulfides in Tannery Wastewaters," J. Am. Leather Chem. Assoc., 67:256-267.

LT-03* Shevchenko, M.A. & R.N. Kas'yanchuk, 1964, "Adsorption of Tanning Substances from Water and Their Stability to Destructive Oxidation", Ukr. Khim. Zh., 30(10):1103-1107.

LT-02

Title: "Oxidation of Sulfides in Tannery Waste Waters"

Authors: J.D. Eye & D.P. Clement

Source: J. Am. Leather Chemists Assoc. 67:256-267 (1972).

Several methods of eliminating sulfide from lime-Na sulfide solutions were studied in laboratory experiments, including NH_4 persulfate (I), ozone, precipitation with $FeSO_4$ (II) and the use of $MnSO_4$ (III), Cr^{+3} (IV) and $KMnO_4$ (V) as catalysts during air oxidation.

Ozone rapidly oxidized the sulfide, as did air when Mn was the catalyst. V was more effective than III. Attempts at removing sulfide with I, II and IV were not successful. The V catalyzed air oxidation reaction then was applied successfully to a wastewater from a hair burning operation which had [sulfide] of 5,000 mg/l. [V] of 500 mg/l provided complete oxidation in 90 min.

In the laboratory study phase, samples containing 100 mg/l sulfide were treated with 100 mg/l V and air, 100 mg/l III with air and with 3.0 and 6.4 standard l/min of ozone (method of generating, contacting and concentrations of ozone in feed gas are not given). In all cases, the final [sulfide] was zero mg/l. Times of contact required to attain complete oxidation of sulfide were: 290 min for V; 1,800 min for III; 180 min for ozone at 6.4 std l/min and 220 min for ozone at 3.0 std l/min.

The authors rejected ozone because it "is only slightly soluble in water and technical problems in efficiently applying this oxidant prevented further study. An efficient contact device might make ozone a feasible means for sulfide elimination, especially in applications where treatment space was limited. Ozone generation equipment currently is expensive and its use must be evaluated carefully".

Costs for sulfide oxidation using V at $0.35/lb were estimated to be $4.25/gal at a wastewater flow of 1,000 gal/day. Two stage aeration would be necessary, and require 1.25 hrs of aeration in stage 1 plus 0.25 hr aeration in stage 2.

Abstractors' Note: Since efficient contacting devices are available for laboratory and full scale ozonation studies, it appears that these investigators were not provided with sufficient technical details regarding contacting by the supplier of the ozonation system employed.

LT-03

Title: "Adsorption of Tanning Substances From Water and Their Stability to Destructive Oxidation"

Authors: M.A. Shevchenko & R.S. Kas'yanchuk

Source: Ukr. Khim. Zh. 30(10);1103-1107 (1964)

It is recommended that ozone and either a coagulant containing 16 to 18% $Al_2(SO_4)_3$ or a 1:1 $Al_2(SO_4)_3$-$FeCl_3$ mixture be used in treating colored waters containing plant extract.

LITERATURE CITED -- MINING (MI)

MI-01* Beller, M. C. Waide & M. Steinberg, 1970, "Treatment of Acid Mine Drainage by Ozone Oxidation", U.S. EPA Report No. EPA-WQO-14010-FMH-12/70, 99 pages. U.S. EPA, Washington, D.C., NTIS No. PB-198,225.

MI-02 Bespamyatov, O.K., A.N. Kvyatkovskii, E.K. Rochin & L.F. Atyaksheva, 1975, "Decomposition of Cyanide-Containing Wastewaters of Concentration Plants by Ozonation with Separate Use of Non-Ferrous Metals", Ref. Zh. Metall.

MI-03 Chernobrov, S.M. & S.M. Rozinoer, 1975, "Ozone Purification of Waste Water from Dressing Plants", Obogashchenie Rud, 20(1).

MI-04 Eiring, L.V., 1967, "Detoxification of Industrial Wastewaters of Gold Mines by Ozonation. I. Behavior of Simple and Complex Anions During Ozonation", Uch. Zap., Erevan, Gos. Univ., 2:49-64.

MI-05 Eiring, L.V., 1969, "Kinetics and Mechanism of Ozone Oxidation of Cyanide-Containing Waste Water", Tsvet. Metal, Nov., p. 42.

MI-06 Fridman, I.D., L.E. Ponchkina, N.N. Khavskii, I.A. Yakubovich & B.A. Agranat, 1969, "Removal of Toxic Cyanides from Wastewaters of Gold Extracting Mills." Sh. Mosk. Inst. Stali Splavov Sbornik, 3:106.

MI-07 Kvyatkovskii, A.N., L.G. Konchina & E.K. Roshchin, 1975, "Possibility of the Use of Catalysts for Purification of Cyanide-Containing Wastewaters with Ozone", Ref. Zh. Metall.

MI-08 Mathieu, G.I., 1975, "Application of the Film Layer Purifying Chamber Ozonation Process to Cyanide Destruction," in *Proc. First Int'l. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning (eds.), Intl. Ozone Assoc., Cleveland, Ohio, p. 533-550.

MI-09 Mathieu, G.I., 1977, "Ozonation for Destruction of Cyanide in Canadian Gold Mill Effluents -- A Preliminary Evaluation", Presented at Symposium on Advanced Ozone Technology, Toronto, Canada, Nov. Intl. Ozone Assoc., Cleveland, Ohio.

MI-10 Rozelle, R.B., *et al.*, 1968, "Studies on the Removal of Iron from Acid Mine Drainage Water", Wilkes College Research & Graduate Center, Wilkes-Barre Penn., Submitted to Coal Research Board, Commonwealth of Pennsylvania.

MI-11 Rozelle, R.B. & H.A. Swain, 1975, "Removal of Manganese from Mine Drainage by Ozone and Chlorine", EPA Report EPA/670/2-75/006. U.S. EPA, Washington, D.C. NTIS Report No. PB-241,143/7WP.

MI-12 Sumitomo Metal and Mining Co., Central Research Dressing Group, 1973, Wastewater Treatment With Ozone at the Konomai Mine", Feb. 12.

MI-13 Swain, H.A., Jr. & R.B. Rozelle, 1974, "Removal of Manganese from Mine Waters", Proc. Fifth Symp. Coal Mine Drainage Research Preprints, 357.

MI-14* Swain, H.A. & R.B. Rozelle, 1975, "Use of Ozone for Treatment of Mine Drainage Discharges", in Proc. First Int'l. Symp. on Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning (eds.), Intl. Ozone Assoc., Cleveland, Ohio, p. 748-753.

MI-01

Title: "Treatment of Acid Mine Drainage by Ozone Oxidation"

Authors: M. Beller, C. Waide & M. Steinberg

Source: EPA Document No. 14010 FMH, 12/70, Water Pollution Control Research Series, 1970. U.S. EPA, Washington, D.C.

Review: An in-depth evaluation of the use of ozone to treat acid mine drainage. Ozone is stable at low pH, thus Fe and Mn can be oxidized at low pH. Other methods depend on raising pH before treatment. In addition, sludge production would be less using ozone.

Ozone Production: Ozone production by means of electrical discharge, isotopic radiation and chemonuclear methods are reviewed. In addition, the economics of ozone production at the point of usage as well as of distribution from a central production facility are presented. Designs for these systems are outlined.

Waste Characteristics: Acid mine drainage flow varied from 25,000 to 6,000,000 gpd with Fe(II) concentrations varying from 50 to 1,000 mg/l.

Cost: The article concludes that the lowest cost process would involve a central plant with ozone generation, distribution systems, high volume acid mine drainage flows and chemonuclear production of ozone. The highest cost process would involve on-site production of ozone via corona discharge, treating low flows. Costs depend upon the amount of Fe and Mn present.

Ozone oxidation combined with limestone neutralization was found to be an effective treatment with relatively simple process control, good removal, reduced sludge handling and costs equal to or less than those of current technology.

References: 40

MI-14

Title: "Use of Ozone for Treatment of Mine Drainage Discharges"

Authors: H.A. Swain & R.B. Rozelle

Source: Proc. 1st Intl. Symp. on Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning, Eds., Intl. Ozone Assoc., Cleveland, Ohio (1975), 748-753.

Review: Mine drainages from both anthracite and bituminous coal mines are characterized by high levels of soluble Fe(II), Mn(II) and acidity. The conventional treatment of lime neutralization and aeration is effective only for the acid and Fe(II) removal, not the Mn(II). This EPA-sponsored research was undertaken to investigate the oxidation of Mn(II) to Mn(IV) and precipitation of Mn(IV) as MnO_2. The variables investigated were initial [Mn], initial [O_3] in the gas stream leading to the reactor, pH and temperature. The rates of Mn removal are as follows:

Variable	Order of dependence	Concentration Range
Mn(II)	1st	<10 mg/l of Mn(II)
Mn(II)	0.5	>10 mg/l of Mn(II)
Ozone	0.5	>2 mg/l of O_3 in gas stream
pH	0.1	
Temp.	0	

At higher pH, lower levels of Mn can be attained (<0.1 mg/l).

Two reactions seem to be occuring with Mn:

(a) oxidation of Mn(II) to Mn(IV),
(b) Mn(IV) reacting with ozone to form a higher oxidation state (permanganate) which becomes soluble.

Ozone reacts with Fe(II) before it reacts with Mn(II). For efficient ozone utilization, removal of the Fe(II) should be accomplished first. Transition metals are more acidic in higher oxidation states and acidity is expected to increase after ozonation.

Chlorine was not found to oxidize Mn(II) at pH values of 1, 3, 5, and 7. Ozone use efficiency was <10%. Further research on ozone contacting is required.

Generator: Model T-23 Welsbach fed by low dew point oxygen.

References: none cited

LITERATURE CITED (ORGANIC CHEMICALS) (OC)

OC-01 Anonymous, 1973, "New Process for Colored Wastewater Treatment", Source Unknown, March 22.

OC-02 Akimova, N.A. & R.A. Karvatskaya, 1968, "Purification of Waste From Organosilicon Production by Ozonation", (Inst. Titan. Zaporozhe, USSR) Khim. PromUgr. 5:48-50.

OC-03 Bauch, H. & H. Burchard, 1970, "Investigations Concerning the Influence of Ozone on Water with Few Impurities", Wasser Luft u. Betrieb 14(7):270-273.

OC-04 Besselievre, E.H., 1957, "The Economical and Practical Use and Handling of Chemicals Used in Industrial Waste Treatment", Proc. 12th Indl. Waste Conf. p. 342-363. Purdue Univ. Engr. Bull., Ext. Serv., No. 94, Lafayette, Indiana.

OC-05 Brower, G.R. 1967, "Ozonation Reactions of Selected Pesticides for Water Pollution Abatement", Wash. Univ., St. Louis, Mo., Ph.D. Diss. #67-9384, 211 pp.

OC-06* Buescher, C.A., J.H. Dougherty & R.T. Skrinde, 1964, "Chemical Oxidation of Selected Organic Pesticides", J. Water Poll. Control Fed. 36(8):1005-1014.

OC-07* Cheremisinoff, P.N., A.J. Pema & E.R. Swaszek, 1975, "Controlling Organic Pollutants in Industrial Wastewaters", Indl. Wastes, Sept./Oct., p. 26-35.

OC-08 Collier, H.E., Jr., 1967, "Recovery of Alkyl Lead Compounds From the Aqueous Effluent From Alkyl Lead Manufacture", U.S. Patent #3,308,061, March 7.

OC-09 Davis, G.M., C.D. Magee, R.M. Stein & C.E. Adams, Jr., 1976, "Ozonation of Wastewaters from Organic Chemicals Manufacture", in *Proc. Sec. Intl. Symp. on Ozone Technol.*, R.G. Rice, P. Pichet & M.-A. Vincent, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 421-435.

OC-10 Farrell, F.C., J.D. Zeff, T.C. Crase & D.T. Boyland, 1977, "Development Effort to Design and Describe Pink Water Abatement Processes", Final Technol. Report No. 1701 to U.S. Army Armament R&D Command, Dover, N.J., August.

OC-11 Fochtman, E.G. & J.E. Huff, 1976, "Ozone-Ultraviolet Light Treatment of TNT Wastewaters", in *Proc. Sec. Intl. Symp. on Ozone Technol.*, R.G. Rice, P. Pichet & M.-A. Vincent, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 211-223.

OC-12 Foshko, L.S. & D.M. Maryanchuk, 1974, "Possibility of Utilization of Sewage Waters at Water Treatment Plants of Power Stations", Terploinergetica (USSR), Jan., p. 72.

OC-13* Gabovich, R.D., J.L. Kurinnyi & Z.P. Fedorenko, 1969, "The Effect of Ozone and Chlorine on 3,4-Benzopyrene During Water Treatment". Gig. Naselennkh Mest., p. 88.

OC-14 Gabovich, R.D. & I.L. Kurinnyi, 1966, in Voprosy Kommunal'noy Gigreny (Questions of Community Hygiene), Kiev, p. 11.

OC-15 Gabovich, R.D. & I.L. Kurinnyi, year unknown, "Ozonation of Water Containing Petroleum Products, Aromatic Hydrocarbons, Nitro Compounds and Organochlorine Pesticides", U.S. Army Medical Intelligence & Information Agency, Rept. No. USAMIIA-K-4567.

OC-16 Gavrilov, M.S., M.Ya. Rozkin, L.V. Storozhenko, G.F. Slezko, V.Ya. Storozhenko & A.A. Chumachenk, 1970, "Use of Ozone to Purify Industrial Discharge", Isv. Vyssh. Uckeb. Zared., Khim. Tekhanol.

OC-17 Goda, T., I. Munemiya & O. Kawahara, 1973, "Ozone Treatment of Secondary Treatment Liquid", J. Japan Sewage Works Assoc. 10(112):14-24.

OC-18* Gorbenko-Germanov, D.S., N.M. Vodop'yanova, N.M Kharina, M.M. Gorodnov, V.A. Zaitsev, A.K. Koldashov & Ya. M. Murav'ev, 1974, "Oxidation of Acetone by Ozone in Aqueous media, as Applicable to the Treatment of Wastewater Containing Ozone", The Soviet Chemical Industry 6(12):756-757.

OC-19* Gregersen, J.K., 1971, "Evaluation of an Ozonation-Activated Carbon Treatment for a Colored Industrial Waste", Thesis, Iowa State Univ., Ames, Iowa.

OC-20 Hoffman, J. & D. Eichelsdörfer, 1971, "Zur Ozone Einwirkung auf Pestizide der Chlorkohlenwasserstoffegruppe im Wasser", Vom Wasser 38:197-206.

OC-21 Hoigné, J., 1975, "Comparison of the Chemical Effects of Ozone and of Irradiation on Organic Impurities in Water", Radiation for a Clean Environment, Intl. Atomic Energy Agency, Vienna, p. 297-305.

OC-22 Il'nitskii, A.P., 1969, "Experimental Investigation of the Elimination of Carcinogenic Hydrocarbons From Water During Clarification and Disinfection", Gig. y Sanit. 9:26-29.

OC-23 Il'nitskii, A.P. & A.Ya. Khesina, 1969, Gig. y Sanit. 6:116.

OC-24 Il'nitskii, A.P., A. Ya. Khesina, S.N. Cherkinskii & L.M. Shabad, 1968, "Vliyanie Ozonirovaniya na Aromatisheskie, v Chastnosti

Kantserogennye, Uglevodorody" ("Effect of Ozonization on Aromatic, in Particular Carcinogenic, Carbohydrates"), Gig. y Sanit. 33(3):8-11. Chem. Abstr. 69:5026X (1968).

OC-25 Ishizaki, K., R.A. Dobbs & J.M. Cohen, 1978, "Oxidation of Hazardous and Toxic Organic Compounds in Aqueous Solution", in *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 210-226.

OC-26 Kalnins, A., *et al.*, year unknown, "Removal of Organic Substances From Industrial Wastewater" Izobret., Prom. Obraztsy, Tovarnye Znaki, 45(24):153.

OC-27 Kandzas, P.F., A.A. Mokina, R.F. Marchenko & L.A. Savina, 1970, "Oxidation of Cyclohexane in an Aqueous Solution Under the Action of Ozone", Tr. Vses. Nauch-Issled. Inst. Vodosnabzh., Kanaliz., Gidrotekh. Scoruzhenii Inzh. Gidrogeol. 28:18-23.

OC-28* Korolov, A.A., 1972, "Ozonation as a Method of Decontaminating Water Contaminated by Chemical Compounds", Gig. y Sanit. 37:78-82.

OC-29* Krasnov, B.P., D.L. Pakul & T.V. Kirillova, 1974, "Use of Ozone for the Treatment of Industrial Wastewaters." Intl. Chem. Engr., 14(4):747-750 (1974). Transl. from Khim. Promy. 1:28-30.

OC-30 Lapidot, H. 1975, "Estimated Cost of Ozone Treatment of an Industrial Wastewater," in *Proc. 1st Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 712-730.

OC-31 LaPlanche, A., G. Martin & Y. Richard, 1974, "Etude de la Dégradation des Pesticides par l'Ozone: Cas du Parathion", Ctre. Belge d'Etude et de Documentation des Eaux 362:22-26.

OC-32 LaPlanche, A., G. Martin & Y. Richard, 1974, "L'Etude de la Dégradation par l'Ozone de Quelques Insecticides du Groupe des Organo-Phosphorés", T.S.M.-l'Eau 7:407-413.

OC-33 Livke, V.A. & S.I. Velushchak, 1971, "Supplementary Ozone Treatment of Wastewaters from Acetylene Production", Khim. Tekhanol. 1:58-60.

OC-34* Livke, V.A., S.I. Velushchak & A.A. Plysynk, 1972, "Ozonation as a Method of Final Purification and Disinfection of Wastewaters That Have Undergone Biological Treatment", The Soviet Chemical Industry 3:156-158.

OC-35 Mallevialle, J., Y. Laval, M. Lefebvre & C. Rousseau, 1978, "The Degradation of Humic Substances in Water by Various Oxidation Agents (Ozone, Chlorine, Chlorine Dioxide) in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 189-199.

OC-36* Mauk, C.E. & H.W. Prengle, Jr., 1976, "Ozone with Ultraviolet Light Provides Improved Chemical Oxidation of Refractory Organics", Pollution Engineering, Jan. p. 42-43.

OC-37 Moldavskii, B.L. & V.K. Tsyskovskii, 1971, "Oxidation of Hydrocarbons--An Economical Way to Produce Petrochemical Products", Khim. I Tech. Top. I Masel 7(5-6):409-413.

OC-38 Oehlschlaeger, H.F., 1978, "Reactions of Ozone with Organic Compounds", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 302-320.

OC-39* Pakul, D.L., A.M. Sazhina & B.P. Krasnov, 1974, "Oxidation of Alcohols in Dilute Aqueous Solutions By Ozone", J. Appl. Chem. USSR 47(1):34-37.

OC-40* Prengle, H.W., Jr., C.E. Mauk, R.W. Legan & C.G. Hewes, III, 1975, "Ozone/UV Process Effective for Wastewater Treatment", Hydrocarbon Processing 54(10):82-87.

OC-41* Prengle, H.W., Jr., C.G. Hewes & C.E. Mauk, 1976, "Oxidation of Refractory Materials by Ozone With Ultraviolet Radiation", in Proc. Sec. Intl. Symp. on Ozone Technol., R.G. Rice, P. Pichet & M.-A. Vincent, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 224-252.

OC-42 Prengle, H.W., Jr. & C.E. Mauk, 1978, "Ozone/UV Oxidation of Pesticides in Aqueous Solution", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 302-320.

OC-43 Reichert, J., 1969, "Examination for the Elimination of Carcinogenic, Aromatic Polycyclics in the Treatment of Drinking Water, with Special Consideration of Ozone." Wasser u. Abwasser 110(18):477-482.

OC-44 Rice, R.G. & G.W. Miller, 1977, "Reaction Products of Organic Materials with Ozone & with Chlorine Dioxide in Water", Presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov., Intl. Ozone Assoc., Cleveland, Ohio.

OC-45 Richard, Y. & L. Brener, 1978, "Organic Materials Produced Upon Ozonization of Water", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 169-188.

OC-46 Robeck, G., K. Dostal, J.M. Cohen & J.F. Kreissl, 1965, "Effectiveness of Water Treatment Processes in Pesticide Removal", J. Am. Water Works Assoc. 57(2):181-199.

OC-47 Rogozhkin, G.I., 1970, Trudy Vsesoyuzn Nauchno - Issled. Inta Vodosnabzheniya, Kanalizatsii, Gidrotekhnicheskikh Sooruzheniy i Gidrogeologii (Works of the All-Union Sci. Rsch. Inst. of Water Supply, Sewerage, Hydraulic Structures & Hydrogeology) 27:45.

OC-48 Sforzolini, G.S., A. Savino & S. Monarca, 1974a, "Decontamination of Water Contaminated with Polycyclic Aromatic Hydrocarbons (PAH) I. Action of Chlorine and Ozone on PAH Dissolved in Doubly Distilled and in Deionized Water", Igiene Moderna 66(3):309-335.

OC-49 Sforzolini, G.S., A. Savino & S. Monarca, 1974b, "Decontamination of Water Contaminated With Polycyclic Aromatic Hydrocarbons (PAH). II. Action of Chlorine and Ozone on PAH Dissolved in Drinking and River Water", Igiene Moderna 66(6):595-619.

OC-50 Sharifov, R.R., L.A. Mamediarova & E.V. Shul'ts, 1973, "Treatment of Wastewaters Containing Petroleum Product", Azer. Neft. Khoz. 53(4):36-38. Chem. Abstr. 70:107925P (1973).

OC-51 Sharonova, N.F., N.A. Kuzmina & Yu.A. Kuhbabin, 1968, "Ozonization of Wastewaters of the Isoprene Industry", Prom. Sin. Kauch.

OC-52 Shevchenko, M.A. & P.N. Taran, 1966, "Products of Ozonization of Humus Materials", Ukr. Khim. Zh. 32(5):532-536. Chem. Abstr. 65:5393h (1966).

OC-53 Shevchenko, M.A., 1965, "Kinetics of Ozonization of Organic Impurities in Natural Waters", Ozonirov. Vody i Vybor Rats. Tipa. Ozonatorn. St., Sb. 37-42.

OC-54 Shkolich, P.W., M.P. Gracheva & E.O. Pen'Kov, 1972, "Carcinogen-Removing Effectiveness of Biological Methods of Purification of Wastewaters from Organic Synthesis Plants", Ref. Zh. Khim., Abstr. No. 23I387.

OC-55* Sigworth, E.A., 1965, "Identification & Removal of Herbicides and Pesticides." J. Am. Water Works Assoc., 57(8):1016-1022.

OC-56 Somiya, I., H. Yamoda & T. Goda, 1977, "The Ozonation of Nitrogenous Compounds in Water", Presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov. 1977. Intl. Ozone Assoc., Cleveland, Ohio.

OC-57 Stepanyan, I.S., I.A. Vinokur & C.M. Padaryan. 1973, "Liquid Phase Oxidation of Phenol, Methanol and Formaldehyde as Applied to Wastewater Purification." Intl. Chem. Engr. 12(14):649-650.

OC-58 Stoveken, J. & T. Sproston, 1974, "Ozone & Chlorine Degradation of Wastewater Pollutants." U.S. Dept. Interior, OWRR Rpt. A-017-VT(1), NTIS Rpt. #PB 238,365/1WP, June. U.S. Dept. of Commerce, Natl. Tech. Info. Service, Springfield, Va.

OC-59 Strackenbrock, K.H., 1958, "Chromatographic Separation of Urochromes and Removal from Water by Ozone", Gesundheits Ingenieur 79:54-55.

OC-60 Tencza, S.J. & R.A. Sierka, 1975, "Ozonation of Low Molecular Weight Compounds". Proc. Second Natl. Conf. on Water Reuse, May 4-8. Am. Inst. Chem. Engrs., New York, N.Y.

OC-61 Tyutyunnikov, B.N., A.A. Drozdov, Z.V. Didenko & S.S. Potatueva, 1968, "Initiation of the Oxidation of a Paraffin by Ozonized Air", Khim. Tekhanol, Topl. Masel 13(2):22-25.

OC-62 Vagobi, V.A., M.S. Gavrilov, V.L. Plakidin, G.F. Siezko & B.A. Ponomarev, 1968, "Ozone Oxidation of Industrial Waste Streams", Vodosnabek. Sanit. Tekh. 4:23-26.

OC-63 Versar, Inc., 1976, "Assessment of Wastewater Management, Treatment Technology and Associated Costs for Abatement of PCB Concentrations in Industrial Effluents", Feb.; "Refinement of Alternative Technologies and Estimated Costs for Reduction of PCBs in Industrial Wastewaters from the Capacitor and Transformer Manufacturing Categories", Jan. 1977; "PCBs in the United States: Industrial Use and Distribution", Feb. 1976. Natl. Tech. Info. Service, Springfield, Va., Rept. No. PB-252,402/3WP.

OC-64 Weil, L., B. Struif & K.E. Quentin, 1977, "Reaktionsmechanismen beim Abbau Organischer Suktanzen im Wasser mit Ozon", Wasser Berlin. *Proc. Intl. Symp.* -- *Ozon und Wasser*, AMK Berlin, Germany (1978), p. 294-307. Intl. Ozone Assoc., Cleveland, Ohio.

OC-65 Wingard, L.B., Jr. & R.K. Finn, 1969, "Oxidation of Catechol to cis, cis-Muconic Acid with Ozone", Indl. Engrg. Chem., Prod. R&D 8(1):65-69.

OC-66 Yocum, F.H., 1978, "Oxidation of Styrene with Ozone in Aqueous Solution", in *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 243-263.

OC-06

Title: "Chemical Oxidation of Selected Organic Pesticides"

Author: C.A. Buescher, J.H. Dougherty & R.T. Skrinde

Source: J. Water Poll. Control Fed. 36(8):1005-1014 (1964)

A laboratory study of the oxidation of the chlorinated hydrocarbon group of pesticides: lindane, aldrin, and dieldrin. Oxidants used were chlorine, peroxide, sodium peroxide, potassium permanganate and ozone.

Equipment: Barber-Coleman Model 10 gas chromatograph, modified to increase sensitivity of electron capture detection system. No ozonator was mentioned.

Experimental Conditions: All experiments were done with distilled, deionized and carbon-filtered water, with pesticide samples allowed to stand 24 hrs. Solutions then were membrane filtered to remove excess pesticide. No attempt was made to quantify the amount of ozone reacting with any of the samples.

Ozone reaction towers were pyrex columns 4 ft (1.2 m) tall and 3 inches (7.6 cm) in diameter with teflon gaskets and teflon-covered end plates. Products of ozonation were extracted twice with pre-purified benzene.

Results: In preliminary studies with 4 hrs contact time, lindane was not removed with chlorine, H_2O_2 or Na_2O_2. $KMnO_4$ and ozone markedly affected lindane concentration but did not completely remove it. Aldrin was completely removed by chlorine [as $Ca(OCl)_2$], was not affected by the peroxides, and was completely removed by permanganate and ozone (3.9% by wt ozonized air at 0.3 l/min--4 hrs contact time).

In more quantitative experiments, lindane required 40 mg/l of permanganate and 24 hrs contact time for about 40% reduction in concentration. Aldrin was completely removed by permanganate at 1 mg/l in 15 minutes of contact.

No attempt was made to obtain the highest utilization of all ozone produced. In fact, in all runs the maximum amount of ozone absorbed into solution was about 10% of the ozone produced. Thus air stripping effects were determined in all ozonation studies.

Aeration had no effect on removal of lindane, but 40 l of ozonized air removed 75% (20 l removed 70%). Aldrin was removed by air stripping and by ozonation (100% by the combustion with 2 to 3 l of ozonized air). Dieldrin was also removed both by air stripping and ozonation (90% with 40 l of ozonized air).

It was postulated that the more volatile the pesticide in water, the easier it can be removed by chemical oxidation.

Lindane was added to Missouri River water in concentrations of 2.2 mg/l and 0.550 mg/l. Ozonation removed 90% of the lindane at dosages of 20 l of ozonized air. Aeration had very little effect.

References: 13

OC-07

Title: "Controlling Organic Pollutants in Industrial Wastewaters"

Authors: P.N. Cheremisinoff, A.J. Pema & E.R. Swaszek

Source: Industrial Wastes, Sept./Oct., 1975, 26-35.

Describes various methods used in the treatment and removal of organic pollutants from industrial wastewater. Variations of each method are included. Biological, physical and chemical treatments were reviewed, including a brief coverage of ozone use. Descriptions were general, giving a broad range of methods rather than an in-depth coverage of any particular one.

Efficiency: About 11 kwhrs of electrical power are needed to produce 1 lb of ozone from air; power requirements are about one-half this amount if pure oxygen is used. Amounts of ozone used to treat each lb of contaminant range from 1.5 to 2.5 lbs.

Contact: Although contact equipment types were not discussed, it is reported that a contact time of 15 min will reduce wastewater organic content from 40 mg/l to around 10 mg/l.

OC-13

Title: "The Effect of Ozone and Chlorine on 3,4-Benzopyrene During Water Treatment"

Authors: R.D. Gabovich, I.L. Kurinnyi & Z.P. Fedorenko

Source: Gig. Naselennkh Mest. (1969), p. 88

Solutions of 3,4-benzopyrene (I) in benzene were added to distilled or tap water (without residual chlorine). Chlorination was conducted with $Ca(OCl)_2$. After treatment with ozone or chlorine, residual I was measured by luminescence spectroscopy at 402.1 nm.

Both chlorine and ozone treatment decreased the amount of I present, but neither completely destroyed it, under drinking water conditions (0.5 to 2 hrs chlorination or 3 to 5 min ozonation). Chlorination reduced [I] 5 to 10 times; ozonation 10 to 50 times.

If water was free of ammonia, chlorination was significantly more effective. At a chlorine dosage of 0.4 to 0.6 mg/l, 4 mkg/l concentrations of I were reduced to 1.0 to 1.3 mkg/l in 30 min, to 0.7 to 0.8 in 2 hrs and to 0.4 to 0.5 in 24 hrs. Overchlorination with 5 mg/l chlorine lowered 4 mkg/l of I to 0.5 mkg/l in 30 min, to 0.4 in 2 hrs, and to 0.2 in 24 hrs. If the water contained <0.5 mkg/l of I, then small dosages of chlorine completely eliminated I in 12 hrs.

It has been proposed [Gref et al., (1953)] that oxidation products of I with chlorine are 5-chloro-I and I-5,8-quinone.

Treatment of water containing 4 mkg/l of I with 2.5 mg/l of ozone for 3 min reduced the level of I to 0.06 mkg/l; 4.5 mkg/l of ozone over 5 min reduced the level of I to 0.04 mkg/l. However, even using large ozone dosages over 10 to 15 min did not decrease I to less than 0.02 mkg/l. Treatment of water containing 0.5 mkg/l of I with 2 mg/l ozone for 3 min reduced the level of I to 0.03 to 0.04 mkg/l. Further increase in ozone dosage was not further effective.

OC-18

Title: "Oxidation of Acetone by Ozone in Aqueous Media, as Applicable to the Treatment of Wastewater Containing Ozone."

Author: D.S. Gorbenko-Germanov, N.M. Vodop'yanova, N.M. Kharina, M.M. Gorodnov, V.A. Zaitsev, A.K. Koldashov & Ya. M. Murav'ev.

Source: The Soviet Chemical Industry 6(12):756-57 (1974).

Primary emphasis is on the methods and equipment employed in oxidation of acetone to CO_2 and H_2O.

Equipment: An undescribed contact device that provided 98% utilization of ozone, whereas only 50 to 70% utilization had been realized previously with methods such as sparging, airlift ejector devices, etc.

Ozonator: OP-66, 11.4 kg/hr. Ozone generated with 960 cu m/hr of air feed at 12 g ozone/cu m concentration.

pH: Close monitoring and control of pH conditions were used in this experiment to realize the complete oxidation of acetone and all of its degradation products to $CO_2 + H_2O$. pH varied from 12.1 to 11.0.

Cost Data: 0.54 ruble/kg (capacity was 10 kg/hr) or 256 rubles (100 cu m/day of acetone).

References: 5

OC-19

Title: "Evaluation of an Ozonation - Activated Carbon Treatment for a Colored Industrial Waste"

Author: Jack K. Gregersen

Source: M. Sci. Thesis, Iowa State Univ., Ames, Iowa, 1971, 114 pages.

Review: Chemical and physical treatment methods that might be effective in removing color from an industrial waste (unidentified) containing aromatic compounds were surveyed. Ozonation eliminated much of the color and some organic carbon. The nature of the ozonized end products was not determined.

Activated carbon is recommended over other techniques because the technology needed to design treatment systems already exists. Ozonation followed by biological treatment is listed second because it is not yet known to what extent the residues from ozonation are truly biodegradable. This process is potentially less expensive to operate than a GAC column.

Ozone Generator: A Welsbach Model T-23 generator operated on oxygen at 0.015 cfm at 8 psi produced 2.9 g/hr of ozone at 5% (by wt) concentration.

Contactor: A fritted glass stick in a 125 ml erlenmeyer flask; 100 ml samples were ozonized.

Experimental: 4 chemical plant (unidentified) wastewater streams were ozonized. These included a combined waste (I), a process waste (II), an As waste (III) and a low pH nitrification process waste containing primarily a salicylic acid derivative. This low pH waste did not appear to be affected by ozone.

In addition, solutions of pure compounds known to be present or related to compounds present in the wastes were ozonized. These compounds included o-nitrobenzoic acid (IV), o-nitroaniline (V), m-nitroaniline (VI), p-nitroaniline (VII), o-nitrophenol (VIII), p-nitrophenol (IX), 3-nitro-4-hydroxyphenylarsonic acid (X) and 4-nitrophenylarsonic acid (XI), all at 200 mg/l in distilled water.

Results: Ozonation of V, VIII, VII and IX produced 9 to 16% organic carbon removal after 90 sec and 18 to 26% removal after 300 sec at pH 8. The rate of ozone application was 7 moles/min/mole of compound consumed. Color removal was observed at 4 wavelengths measured, but an increase in color was observed at 470 nm for VII and at 500 nm for IX.

Both IV and XI (colorless before ozonation) became colored after ozonation, but lost some organic carbon. VI increased in color at all 4 wavelengths during the first 300 sec of ozonation, but after 600 sec the color had begun to fade. The color of X was almost completely removed after 600 sec (3.8-6.8 moles ozone/min/mole of X). III was only slightly less colored after 600 sec of ozonation than before. Samples of I and II lost considerable color after 600 sec of ozonation, and the pH dropped from 9.9 to 8.1 (probably caused by loss of ammonia).

The following changes in organic carbon content (in mg/l) were observed upon ozonation 300 seconds: V, pH 6 or 8, 102 to 81 mg/l; V, pH 10, 102 to 90; VII, pH 8, 99 to 80.5 mg/l; pH 10, 99 to 83; VIII, pH 8, 97 to 79.5 mg/l; pH 10, 97 to 75; IX, pH 8, 100 to 74 mg/l; pH 10, 100 to 75.5; IV, pH 8, 97.5 to 84 mg/l; pH 10, 97.5 to 82.

OC-22

Title: "Experimental Investigation of the Elimination of Carcinogenic Hydrocarbons"

Author: Il'nitskii, A.P.

Source: Gig. y Sanit. (Hygiene and Sanitation) 9:26-29 (1969).

Review: The methods of elimination of carcinogenic polycyclic aromatic hydrocarbons from water were investigated, including flocculation, filtering, chlorination, UV irradiation, and ozonation. Benzpyrene was destroyed by ozone so rapidly that its concentration was reduced approximately 200 times in 5 min, from an original concentration of 3.7×10^{-8} to 1.2×10^{-6} g/ml. Unmodified benzpyrene could no longer be detected after 7.5 minutes.

Procedure: An acetone solution of benzpyrene was poured into 1-liter jars. After the solvent was evaporated, a jar was filled with 1 liter of pond water (40 to 50 mg/l of suspended matter; pH 7.4; temperature 15 to 18°C), and the contents were mixed on a rocker for 30 min. The ozone-oxygen mixture was bubbled through the solution for both 5 and 7.5 min. The effect of ozone was then stopped by the addition of 0.1N sodium hyposulfite.

References: 6

OC-28

Title: "Ozonation as a Method of Decontaminating Water Contaminated by Chemical Compounds"

Author: A.A. Korolov

Source: Gig. i Sanit. 37:78-82 (1972)

Review: A literature review, concentrating on the effects of ozone on different kinds of chemical compounds in industrial wastewater. The topics covered include:

1) Phenols. Using ozone doses from 1 to 1.84 g/l, the concentrations of phenol in aqueous solution were lowered from 95-440 mg/l to 0.05-0.08 mg/l. COD levels were reduced 10 to 20 times (V.I. Khanagbeyev). For effective disintegration of high concentrations of phenol, huge ozone doses (of 1 to 2.5 g/l) were necessary. Complete oxidation may prove economically unfeasible (H.R. Eisenhauer), with 98% disintegration of phenols in water using 4.5 moles ozone/mole of phenol. The relative amounts of ozone needed increased with the degree of phenol destruction: 40% destruction requires 0.75 mg ozone/mg phenol, 90% destruction - 1.85 mg ozone/mg phenol, and 98% destruction - 2.35 mg ozone/mg phenol (R.D. Gabovich). Ozonation of aqueous phenol results in initial cleavage of the benzene ring (3 moles ozone/mole phenol), followed by direct oxidation forming glyoxylic, acetic, maleic, oxalic, carbonic and other acids (2.5 moles oxygen/mole phenol) (H. Bauch et al.).

2) Petroleum Products. Petroleum products from refining plants in concentrations of 300 mg/l experienced 50% destruction from an ozone dosage of 75 mg/l (N.V. Sokolova). Long periods of time were needed for treatment (M.A. Popov). With a concentration of 20 to 30 mg/l of petroleum products passing preliminary purification in buffer ponds, 2 to 3 hrs of ozonation were required.

3) Cyanides. The effectiveness of CN^- destruction significantly increased under the influence of catalysts, Cu in particular (Sondak & Dodge). The effectiveness especially increased at pH 12.0.

4) Organophosphorus Pesticides. Ozone actively oxidized carbophos, methaphos, M-81, and trichlormethaphos-3. Complete destruction of carbophos at a concentration of 10 mg/l occurs using 26 mg/l doses of ozone. Net 8 to 10 mg/l doses of ozone reduce initially equal concentrations of trichlormethaphos-3, methaphos, and M-81 to 0.7, 0.1, and 0.0 mg/l, resp. (R.D. Gabovich & I.L. Kurinnyi).

5) Varied Organic Synthetic Compounds. Dimethylamine in an alkaline wastewater was ozonized to HCHO, formic and carbonic acids, nitrites and nitrates, and under certain conditions, to only CO_2 and nitrates (G.I. Rogozhkin). 90 min of ozonation of cyclohexane at a concentration of 50 mg/l, using 5 to 7 mg ozone/mg cyclohexane, and at pH 11.5 to 12.5, resulted in a COD decrease from 120 mg/l to 5.95-13 mg/l, with the cyclohexane being oxidized almost completely to CO_2.

References: 50

OC-29

Title: "Ozonization of Industrial Wastewater"

Authors: B.P. Krasnov, D.L. Pakul & T.V. Kirillova

Source: Khim. prom. 1:28-30(1974). English translation in Intl. Chem. Engrg. 14(4):747-750 (1974).

Ozonation of ethanol (a model compound for aliphatic alcohols) was studied in dilute aqueous solutions. Glass columns 40 and 60 mm in diameter and 400 mm tall were used. Ozonized air was cleaned of nitrogen oxides by passing through a dilute alkaline absorber, then entered the contact column through a 40-50 μ pore size filter. The mixture contained 33 mg/l of ozone. Oxidation products were measured by gas chromatography.

In all cases except MeOH (EtOH, BuOH and octanol) the final oxidation products were alcohols, which were formed from aldehyde intermediates. CO_2 was not observed to form in any case. The rate of oxidation increased with increasing pH, and the rates of oxidation of all alcohols are practically identical for various initial and almost equal final pH values.

Ozonation of secondary alcohols gave organic acids, but with ketones as intermediates, and H_2O_2 is formed at the same time. The intermediate oxidation products were lower boiling than the original materials and were readily transferred to the gaseous phase.

Because of the low bond energy of oxygen atoms in ozone (24 kcal/mole), the reactions are assumed to proceed through free radical mechanisms. Formed hydroxy radicals produce hydroperoxides which are unstable and decompose to aldehydes (in the case of primary alcohols) or ketones (secondary alcohols). Aldehydes are oxidized to peracids which, in dilute aqueous solution, decompose to organic acids and H_2O_2. Material balances showed that ozone consumption is higher at alkaline pH and H_2O_2 does not build up.

The limiting stage of oxidation is initiation, and its rate rises in alkaline media, due to the increased formation of radicals. Formation of peroxides upon ozonation of wastewater (which decompose to radicals) thus is a positive factor. Production of acids also is a positive factor, since they (and other partially oxidized intermediates) are more readily biodegraded than the initial alcohols. Thus a decrease in COD and an increase in BOD should be expected.

Gases exiting the contactor should be cleaned of volatile oxidation products before release to the atmosphere.

OC-34

Title: "Ozonation as a Method of Final Purification and Disinfection of Wastewaters That have Undergone Biological Treatment"

Authors: V.A. Livke, S.I. Velushchak and A. A. Plysynk

Source: The Soviet Chemical Industry 3:156-158 (1972)

Laboratory and pilot ozonation studies were conducted on wastewaters from organic chemicals manufacture which had been subjected to secondary biological treatment.

Ozone was generated from air or from oxygen and the gas was fed through a porous plate. Wastewaters from caprolactam synthesis (Shchekino and Serverodonetsk Chemical Works) after secondary treatment and after ozonation had the properties listed in Tables 5 and 6.

TABLE 5. OZONE TREATMENT OF SERVERODONETSK CHEMICAL WORKS, BIOLOGICALLY TREATED WASTEWATERS

parameter	after secondary treatment	after ozone treatment		
		ozone consumption (mg/l)		
		10	15	20
COD(mg O_2/l)	92	82	74	68
BOD	11	13	16	24
BOD-5(mg O_2/l)	78	30	30	25
DO	5.2	5.0	4.5	4
NH_3	0.25	0.05	traces	not detected
nitrites	4.5	4.6	4.8	5.1
nitrates	24	13	9	traces
microbe no. 1 0_3 os/ml	6.2	5.0	3.0	2.4
Coliform titer	0.004	0.04	0.43	0.43

TABLE 6. OZONE TREATMENT OF SHCHEKINO CHEMICAL WORKS, BIOLOGICALLY TREATED WASTEWATERS

Parameter	after secondary treatment	after ozone treatment				
		ozone consumption (mg/l)				
		5	10	15	20	25
COD(mg O_2/l)	120	106	96	92	56	42
BOD-5(mg O_2/l)	9.7	13	16	17	22	23
DO mg/l	3.5	12.8	25.8	26.4	27.0	29.1
NH_3, mg/l	15.9	15.9	15.4	14.7	14.3	13.5
nitrite mg/l	0.5	0.2	0.11	0.1	none	none
nitrates mg/l	14.7	14.8	15.3	16.0	16.8	17.4
urea mg/l	7.3	6.2	4.9	none	none	none
caprolactam mg/l	2.8	1.2	0.9	0.5	none	none
hydroxylamine mg/l	0.9	0.1	none	none	none	none
cyclohexanol mg/l	0.7	0.5	none	none	none	none
Microbe no, 1 0_3 os/ml	30	22	4	1.5	none	none
Coliform titer	0.004	0.004	0.04	0.43	4.3	4.3

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Complete clarification of wastewaters is achieved at an ozone consumption of 10 mg/l. Increasing ozone consumption to 15 to 25 mg/l contributes to complete removal of resins as a result of oxidative decomposition to simpler compounds. This is indicated by the fact that BOD increases while COD decreases with increasing ozone consumption.

Following a period in biological ponds, the ozonized water can be reused. The cost of ozonizing biochemically purified wastewaters for recycle and reuse is about 15% of the cost of biochemical purification.

References: 6

OC-36

Title: "Ozone with Ultraviolet Light Provides Improved Chemical Oxidation of Refractory Organics"

Authors: C.E. Mauk & H. W. Prengle, Jr.

Source: Pollution Engineering, Jan. 1976, 42-43.

Laboratory investigation of the ozone/UV oxidation of ethanol, glycerol, acetic acid, glycine and ammonium palmitate (100 mg/l and below in deionized water) is reported.

The treatment system consists of 3 stirred staged reactors, each having UV light added, in which solution flows countercurrent to the ozone flow.

In the absence of UV radiation, the ozone autodecomposition rate constant was 0.2 lb mole/cu ft-min and the equilibrium ozone concentration of 14 mg/l was reached. When UV radiation was added the ozone autodecomposition rate constant increased to 8 lb mole/cu ft - min and the equilibrium ozone concentration fell to 2 mg/l. TOCs of all test solutions were quickly reduced to below the detectable limits (times not given). UV activates not only the 1st step but also the further oxidation of intermediate products.

There are several advantages of a multistage reaction system over a single stage reactor. When each stage is optimized in terms of pH, mixing, residence time, temperature and UV intensity, the total residence time will be minimum, reducing total equipment size. Sufficient UV should be used to increase the chemical reaction rate so that mass transfer of ozone becomes the limiting factor.

OC-39

Title: "Oxidation of Alcohols in Dilute Aqueous Solutions By Ozone"

Authors: D.L. Pakul, A.M. Sazhina & B.P. Krasnov

Source: J. Appl. Chem. USSR 47(1):34-37, 1974

Ozonization of wastewaters containing considerable amounts of various alcohols has been studied. Ozonization of normal aliphatic alcohols in aqueous solutions forms the corresponding aldehydes and acids. The surface tension of alcohol solutions is 1 of the factors determining the oxidation rate. The ozonization method may be used for treatment of wastewaters containing butanol and higher alcohols.

References: 6

OC-40

Title: "Ozone/UV Process Effective Wastewater Treatment"

Author: Prengle, H. W. Jr., C. E. Mauk, R. W. Legan & C. G. Hewes, 111

Source: Hydrocarbon Processing, Oct. 1975, 82-87

Combining UV radiation with ozone treatment produces a synergism which allows normally refractory (to ozone oxidation) compounds to oxidize rapidly. UV radiation enhances ozone reaction rates by 10^2 to 10^4 fold, and drives the reactions to completion to CO_2, water, etc. Compounds whose oxidation reaction rates are too slow to be economical (alcohols, acids, amino-acids and polyhydroxyaliphatic alcohols) with ozone alone now can be rapidly and economically oxidized. Refractory toxic materials, such as K ferricyanide, also are oxidized rapidly.

Oxidation reaction rates with ozone also can be increased by addition of heat, but use of UV (6 watt/l for acetic acid) is more effective than elevating temperature, and requires less energy.

UV radiation of organics produces free radicals, and the rates of oxidation of these are more rapid than those of the parent molecules. UV also catalyzes the autodecomposition of ozone---perhaps to more reactive oxygen species.

Time of contact with ozone can be shortened significantly by addition of UV radiation. This will save energy of generating ozone for the excess time of contact, but will require a small increment of energy for the added UV radiation.

Details of reactor design are not given. However, more easily oxidized materials are treated in a single stage ozone/UV reactor, the more refractory compounds are oxidized in a 2nd multi-staged reactor.

For example, a wastewater containing 900 mg/l of TDS including free and complexed cyanides and refractory organics can be treated to reduce total CN^- to below detectable limits (<0.1 mg/l) and TOC to <1 mg/l by coagulation with alum, activated silica and polyelectrolyte, sedimentation, clarification and equalization. After adjusting the pH to 7 to 8, a single stage ozone/UV reactor (operating on air) is followed by a multistage ozone/UV reactor. To treat 500 tons/day (83.3 gpm) requires an installed plant cost of $590,000, with operating costs, including amortization, of $500/day.

To treat 700 tons/day (117.4 gpm) of wastewater containing ammonia, CN^- and organic nitrogen compounds (1,000 mg/l total N) to dischargable levels requires pH adjustment (basic), steam stripping of ammonia, neutralization, and treatment with ozone/UV in 2 stages.

The ozone generators use recycled oxygen. Installed plant cost is $334,000, and operating costs are $225/day.

Refractory organics remaining in sewage after secondary treatment and activated carbon can be removed using ozone/UV. A 1 mgd stream containing 10 mg/l of TOC (to be reduced to below 0.1 mg/l is treated in a multistage ozone/UV reactor (ozone from air). Organics are converted to CO_2 and water. Ozone concentration is adjusted automatically by an effluent monitor. Installed plant cost is $505,000. Reactor staging allows more than 67% cost savings over single stage treatment costs.

OC-41

Title: "Oxidation of Refractory Materials by Ozone with Ultraviolet Radiation"

Authors: H.W. Prengle, Jr., C.G. Hewes, III & C.E. Mauk

Source: Proc. Sec. Intl. Symp. on Ozone Technology, R.G. Rice, P. Pichet & M.-A. Vincent, Editors, Intl. Ozone Assoc., Cleveland, Ohio, 1976, p. 224-252.

Review: The authors studied the rates of oxidation of refractory chemical species with ozone and UV light. These included ethanol, acetic acid, glycine, glycerol and palmitic acid. The molecules were graded according to difficulty of oxidation by a Refractory Index Scale (RFI), with a larger RFI indicating more difficulty in oxidation. The specific compounds tested were rated 245, 1,000, 19.7, 112 and 27.3, resp.

Ozone alone was not particularly effective as an oxidant for these chemicals. The simultaneous use of UV radiation, however, increased the oxidation rate 100 to 1,000 fold and drove the reactions to completion. With a small amount of UV radiation the chemical reaction rates were the rate-controlling factors; with larger amounts of UV, however, the reaction rates became mass transfer controlled. More small free radicals were formed, which were oxidized directly to such molecules as CO_2 and H_2O.

Ozonation combined with UV radiation is theorized to be a 2-step process: photochemical excitation by UV, followed by oxidation by ozone. EtOH was oxidized to the intermediate HCHO, then to acetic acid, and finally to an alcohol plus CO_2. In the limiting case of 1-carbon chains, water was formed.

The use of UV radiation led to substantially more free radicals being formed than did the use of ozone alone, which radicals initiated many more propagation chains.

Elevated temperatures enhanced the reaction rates, but not as dramatically as did additional UV. The difference between the reaction at 30°C and at 50°C was not great and indicated that still higher temperatures would have little effect.

Mass transfer data were independent of the chemical reaction. When the reactor was operated with "complete mixing" (500 to 800 RPM), without UV, the equimolar ozone concentration was 12 to 14 mg/l, the mass transfer coefficient about 1.4 (lb mols ozone/cu ft min), and the auto-decomposition constant in the range of 5 to 20% of the mass transfer coefficient. With UV radiation, under the same conditions, the equilibrium ozone concentration was about 2 mg/l, the mass transfer coefficient.

Ozone Generator: The ozone generator was not described.

Contact: A continuously sparged 9.92 l batch stirred tank reactor, served as the reaction vessel. The sparging gas was oxygen with 1 to 5 wt% of ozone. The UV lamp used was a General Electric germicidal bulb. Part of the UV energy emitted at a wavelength of 254 nm, and a useful UV output of 0.55 watt/l of reactor liquid. UV light was irradiated into the stirred reaction mixture at the same time that ozone was being sparged.

Economics: Economic factors were not discussed.

OC-55

Title: "Identification & Removal of Herbicides and Pesticides"

Author: E. A. Sigworth

Source: J. Am. Water Works Assoc. 57:1016-1022 (1965).

Reviews work of Robeck et al., J. AWWA 57:181 (1965) utilizing coagulation, oxidation with chlorine, chlorine dioxide, ozone and $KMnO_4$, and adsorption with activated carbon.

Coagulation with alum and iron salts demonstrated partial removal of a few products tested (DDT was removed very effectively). Oxidation studies showed little merit in chlorination or $KMnO_4$. Ozone was more effective than chlorine dioxide on only a few of the products tested. In at least 1 case the oxidized product was "far more toxic" than the untreated insecticide. The basis for this statement was not presented.

All studies to date have shown that activated carbon has been successful in reducing the concentration of the few herbicides and insecticides tested to date, including benzene hexachloride, DDT, 2,4-D, toxaphene, dieldrin, aldrin, chlordane, malathion and parathion.

LITERATURE CITED (PAINT & VARNISH) (PV)

PV-01 Ballnus, W. & W. Leiss, 1968, "Verfahren zur Behandlung von Abwässern der Lackindustrie" (Procedures for Treating Wastewaters of the Varnish Industry), Wasser, Luft und Betrieb 12(5):289, 292-293.

PV-02* Bauch, H. & Burchard, H., 1970, "Experiments to Improve Highly Odorous or Harmful Sewage with Ozone", Wasser, Luft & Betrieb, 14(4):134-137.

PV-03 Kroop, R.H., 1973, "Treatment of Phenolic Aircraft Paint Stripping Wastewater", USAFWL Rept. 72-181, Jan., 98 pp. U.S. Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico.

PV-04* Kroop, R.H., 1975, "Ozonation of Phenolic Aircraft Paint Stripping Wastewater", in *Proc. First Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, Editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 660-673.

PV-02

Title: "Experiments to Improve Highly Odorous or Harmful Sewage with Ozone"

Authors: H. Bauch & H. Burchard

Source: Wasser, Luft und Betrieb 14(4):134-137 (1970)

Wastewaters from a German paint and varnish plant were tested by various techniques before discharge. Flocculation then filtration through activated carbon was acceptable for small volumes of wastewater, but for large volumes the cost of activated carbon was too high. Furthermore, it could not be regenerated because of fouling by the adsorbed organics. Treatment with H_2O_2 also was acceptable for small volumes of wastewater, but also was too expensive for large volumes. Chlorine oxidation was unacceptable because chlorinated organics were produced which interfered with biological processes during later clarification.

Ozone Generator: GOTA (Gesellschaft für Ozon Technik und Andwendung GmbH, Düsseldorf, Federal Republic of Germany). Ozone was prepared from air or oxygen.

Contactor: A standing glass tube 2 m long, 40 mm diameter, with G-3 frit. Volume of sample treated was 1.5 l.

Wastewater from a varnish plant was preclarified with $FeCl_3$ and/or $Al_2(SO_4)_3$, then neutralized. Ozonation then was conducted by passing 20 mg/l ozone in air for 30 min at 19°C. Results obtained are given in Table

7. Sulfides and Fe(II) were oxidized, the organic odors were decreased considerably, the residue on evaporation was decreased by 9% (210 mg/l) but the residue upon ignition remained the same. These data indicate that organics were oxidized to CO_2 by the ozone. In addition, $KMnO_4$ oxidizability was lowered from 1,940 to 340 mg/l, BOD-5 level was reduced from 1,400 to 190 mg/l and volatile hydrocarbons, volatile phenols, non-volatile phenols and fats and oils also were reduced in concentration.

Even better results were obtained when the wastewaters were pretreated with chlorine, which was not as effective without subsequent ozonation (see Tables 8 and 9). Ozonation will convert residual chlorine to perchlorate, which also is a powerful oxidant. These tables also show experiments using hot and cold aeration, which gave some improvement, but which was not sufficiently effective.

TABLE 7. TREATMENT OF SEWAGE OF A VARNISH PLANT BY GASSING WITH OZONE (20 MG O_3 IN AIR) FOR 30 MINUTES AT 19°C

Analytical Parameters	Before treatment	After treatment
Capable of settling after 2 hrs	6 ml/l	6.3 ml/l
Appearance after settling	slightly turbid, yellow	slightly turbid, almost colorless
Odor	intensively of varnish	stale, faintly of varnish
Odor threshold	1:600	1:16
pH value	6.0	5.3
Conductivity in microsec	4,900	4,950
Residue on evaporation	2,400 mg/l	2,190 mg/l
Residue on ignition	1,010 mg/l	1,040 mg/l
Chlorides as Cl	150 mg/l	155 mg/l
Sulfate as SO_4	320.0 mg/l	335 mg/l
Sulfide as H_2S	8.0 mg/l	not traceable
Overall hardness in ° dH	15.6 mg/l	14.2 mg/l
Calcium as CaO	128.0 mg/l	130.0 mg/l
Iron II	20.0 mg/l	not traceable
Iron III	11.0 mg/l	36.0 mg/l
Zinc as Zn	131.0 mg/l	135.0 mg/l
Lead as Pb	18.0 mg/l	16.0 mg/l
Copper as Cu	3.5 mg/l	3.0 mg/l
Volatile hydrocarbons	140.0 mg/l	20.0 mg/l
Volatile phenols	24.0 mg/l	4.0 mg/l
Nonvolatile phenols	14.0 mg/l	not traceable
Fats and Oils	62.0 mg/l	32.0 mg/l
Oxidizability ($KMnO_4$ consumption)	1,940.0 mg/l	340.0 mg/l
BOD-5	1,400.0 mg/l	190.0 mg/l

TABLE 8. WASTEWATER DISCHARGE OF A PAINT & VARNISH PLANT TREATED 25 MINUTES WITH OZONIZED AIR*

	Appearance	Odor	Odor Thresh-old	$KMnO_4$ Con-sumption	BOD-5 mg/l	Lead mg/l	Zinc mg/l	Volatile Components mg/l	Fats & Oils mg/l
Untreated sewage after 24 hrs settling	milky turbid, brownish	intensively of varnish and esters	1:1,000	2,850	1,860	40.0	200	80	98
Sewage acidified with sulfuric acid (pH 3.6) addition: 0.05 g iron as $FeCl_3$ + 0.05 aluminum as $Al_2(SO_4)_3$, neutralized milk of lime up to pH 8.1	clear yellowish	intensively of varnish and esters	1:900	2,800	1,900	--	--	80	15
Clarified sewage gassed cold with air	clear yellowish	intensively of varnish and ester	1:500	2,400	1,600	--	--	30	14
Clarified sewage gassed hot with air	clear yellowish	intensively of varnish, faintly of ester	1:150	1,400	1,050	--	--	15	16
Clarified sewage treated with ozone	clear yellowish	faintly of varnish	1:18	110	180	--	--	--	16
Clarified sewage pretreated with Cl_2, then treated with ozone	clear, strongly yellowish	stale, somewhat of benzene	1:8	120	80	--	--	--	12

* 20 mg ozone/liter of air

Source: Bauch & Burchard, 1970

TABLE 9. WASTEWATER FROM THE CANAL NEAR THE OUTLET OF A PAINT & VARNISH MANUFACTURING PLANT, PRETREATED BY PRECIPITATION AND TREATED WITH OZONE* (30 MINUTES) AND CHLORINE

	Appearance	Odor	Odor Thresh-old	$KMnO_4$ Consumption mg/l	BOD-5 mg/l	Lead & Zn mg/l	Volatile Portions mg/l	Fats and Oils mg/l
Untreated sewage after 24 hrs settling	milky, turbid	intensively of varnish	1:800	3,850	1,800	114.3	110	80
Sewage acidified to pH 5.0 with sulfuric acid addition: 0.1 g/l iron as $FeCl_3$, precipitated with milk of lime at pH 7.6	clear yellowish	intensively of varnish	1:700	2,900	2,600	traces	70	18
Clarified sewage gassed cold with air	clear yellowish	intensively of varnish	1:500	2,720	2,100	traces	60	16
Clarified sewage gassed hot with air	clear yellowish	intensively of varnish	1:240	1,800	1,400	traces	10	19
Clarified sewage gassed cold with ozonized air	clear, almost colorless	faintly of varnish	1:20	190	260	traces	--	16
Clarified sewage pretreated cold with excess Cl_2, then ozonized air	clear, almost colorless	stale, indefinable	1:4	82	150	traces	--	5

* 20 mg ozone/liter of air

Source: Bauch & Burchard, 1970

PV-04

Title: "Ozonation of Phenolic Aircraft Paint Stripping Wastewater"

Author: R. H. Kroop

Source: Proc. First Intl. Symp. on Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning, editors. Intl. Ozone Assoc., Cleveland, Ohio (1975), p. 660-673.

Aircraft paint stripping wastewaters contain 1,000 to 3,000 mg/l of phenols, 1,000 to 3,000 mg/l of CH_2Cl_2, 5,000 to 30,000 mg/l of COD, 50 to 200 mg/l of Cr, 100 to 1,000 mg/l of SS, 100 to 2,000 mg/l of oils and have pH in the 8.0 to 8.5 range. Some 71.5% of the COD is contributed by phenols.

In batch ozonation experiments with a wastewater containing 2,700 mg/l phenol, 99.7% of the phenol was destroyed in 1 to 2 hrs, but COD values were reduced only 57%. CO_2 formation was not substantial, (10% of stoichiometric) thus intermediate oxidation products probably were formed which were not detected by the 4-aminoantipyrine method for phenol. When the pH (8.1) was not controlled, the ozone/phenol demand was 10.4 moles/mole or 5.30 g/g. At an initial pH of 11.0, this ratio was lowered to 3.46 moles/mole or 1.77 g/g. Reduction of COD levels during the first 30 min of ozonation was caused by air stripping of CH_2Cl_2. Concentrations of ozone were measured in the gas phases before and after ozonation.

Continuous flow tests were made using 2-stage ozone contacting at an influent pH of 11.5. Ozone feed rate to diffuser reactor #1 was 2,000 cc/min at 40 mg/min of ozone, and an additional 1,000 cc/min at 17 mg/min to diffuser reactor #2. All 40 mg/min of ozone charged to reactor #1 was consumed in reactor #1. Wastewater flowed through the 2 reactors consecutively. To attain 99% destruction of phenol (first order reaction) required approximately 200 min (30 mg/l residual phenol) and to attain 99.9% destruction (3 mg/l residual phenol) required approximately 300 minutes of ozonation.

After 240 minutes of ozonation, even though the [phenol] was <20 mg/l, the [COD] was 3,500 mg/l (65% reduction). To attain 99% phenol removal required 5.2 moles ozone/mole phenol (2.66 g/g); to attain 99.9% removal required 8.0 moles/mole (4.50 g/g).

Costs: Capital and operating costs to treat 29,000 gpd of phenolic aircraft paint stripping wastewater by ozonation were estimated for 2 different levels of treatment as follows:

	[phenol]	
	20 mg/l	2.0 mg/l
Capital cost	\$389,000	\$505,000
Operating cost	\$400/day	\$548/day

References: 10

LITERATURE CITED (PETROLEUM REFINERIES) (RE)

RE-01 Alekseeva, V.A., 1965, "Use of Ozone in Purification of Wastewater", Khim Tekhnol, Topliv i Masel.

RE-02* Alekseeva, V.A. & Ya.A. Karelin, 1963, "The Purification of Petroleum Refinery Wastewaters with Ozone." Neftepererabotka i Neftekhim., Nauchno-Teknicheskii Sbornik, 5:19-21.

RE-03* Anonymous, 1973, "Ozone Cleans Bug-Ridden Oil", New Scientist, March, p. 548.

RE-04* Anonymous, 1974, "Disposal, Regeneration and Recovery of Used Industrial Oils", Machine Moderne, Nov., p. 38-45.

RE-05 Anonymous, 1957, "Removal of Phenols From Refinery Wastes", Oil in Canada, June 24, p. 26.

RE-06* Dabine, R.A., 1959, "Phenol Free Wastewater." Chem. Engrg., Aug. 24, p. 114-117.

RE-07* Diehl, D.S., R.T. Denbo, M.N. Bhatla & W.D. Sitman, 1971, "Effluent Quality Control at a Large Oil Refinery." J. Water Poll. Control Fed. 43:2254-2270.

RE-08 Diehl, D., 1976, "Ozone for Taste & Odor Control of a Refinery Effluent", in Ozone: Analytical Aspects & Odor Control, R.G. Rice & M.E. Browning, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 77-78.

RE-09 Filby, J., J. Hutcheon & R. Schutte, 1976, "Use of Ozone in the Preparation of Industrial Boiler Feed Water", in Forum on Ozone Disinfection, E.G. Fochtman, R.G. Rice & M.E. Browning, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 337-343.

RE-10* Gabovich, R.D. & I.L. Kurinnoi, 1967, "Ozonization of Water Containing Petroleum Products, Aromatic Hydrocarbons, Nitro Compounds and Chloro-organic Pesticides." Gig. Naselennykh Mest., (USSR) Izd. "Zdorov'ya", p. 31-35.

RE-11* Hoffman, T.W., D.R. Woods, K.L. Murphy & J.D. Norman, 1973, "Simulation of a Petroleum Refinery Waste Treatment Process", J. Water Poll. Control Fed. 45(11):2321-2334.

RE-12* Ioakimis, E.G., A.E. Kulikov, V.I. Nazasov, N.M. Podgoretskaya, & S.O. Eigenson, 1975, "Use of Ozone in Treating Refinery Wastes", Chem. Technol. Fuels Oils 11(3-4):188-192.

RE-13 Korolev, A.A., Yu.P. Tikhomirov & P.E. Shkodich, 1972, "Use of Ozone for Decontamination of Carcinogenic Waste Waters Containing

Petroleum Products." Vop. Profil Zagryazneniya Okruzhayushch. Cheloveka Sredy Kantserogen. Veshchestvami, p. 72-75.

RE-14* Malkina, I.I., 1971, "Ozone Oxidation of Demulsifiers Present in Wastewaters From Petroleum Refineries and an Evaluation of the Toxicity of the Treated Water". Sb. Tr., Mosk. Inzh. Stroit. Inst. 87:133-136. Chem. Abstr. 78:151232p.

RE-15* McPhee, W.T. & A.R. Smith, 1962, "From Refinery Wastes to Pure Water", Engrg. Bull., Purdue Univ. Engrg. Ext. Ser. 109:311-326.

RE-16* Murdock, H.R., 1951, "Ozone Provides an Economical Means for Oxidizing Phenolic Compounds in Coke Oven Wastes", Indl. Engrg. Chem. 43(11):125A, 126A, 128A.

RE-17 Niegowski, S.J. 1956, "Ozone Method for Destruction of Phenols in Petroleum Wastewaters", Sewage & Indl. Wastes 28:1266-1272.

RE-18* Peppler, M.L. & G.R.H. Fern, 1959, "A Laboratory Study on Ozone Treatment of Refinery Phenolic Wastes". Oil in Canada 11(27):84-90.

RE-19 Popov, M.A., 1970, "Purification of Petroleum Wastewaters by Ozonization", Trudy Vses. Nauchno-Issled Dovatel'skii Inst. Vodo Snab Sehenii Kanalizatsii, Gidrogeologii 2:45-48.

RE-20* Popov, M.A., 1960, "Use of Ozone for the Final Treatment of Effluents From an Oil Refinery", Gig. y Sanit. 25(5):92-93.

RE-21 Schafer, C.J., 1977, "Petroleum Refining and Organic Chemicals: Canada". U.S. Environmental Protection Agency, Effluent Guidelines Division, Trip Report, March.

RE-22* Sease, W.S. & G.F. Connell, 1966, "Put Ozone to Work Treating Plant Wastewater", Plant Engineering, Nov.

RE-23 Sharifov, R.R., Sh.I. Ismailov, S.S. Korf & A.R. Mamedova, 1976, "Purification of Petroleum-Containing Formation Waters by Ozonization and Sorption". Tr. Vnii Vodosnabzh, Kanaliz, Gidrotekhn. Sooruzh. I Inzh. Gidrogeol. Bakin. Fil., 12:18-22.

RE-24 Sharifov, R.R., L.A. Mamed'yarova & E.V. Shul'ts, 1973, "Treatment of Wastewater Containing Petroleum Products". Azer. Neft. Khoz. 53(4):36-38.

RE-25 Shevchenko, M.A., Yu.M. Kaliniichuk & R.S. Kas'yanchuk, 1964, "Purification of Water from Phenols and Petroleum Products by Ozonization." 'Kr Khim. Zh.

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RE-26* Tungfanghung Oil Refinery; Tsinghua Univ., 1975, (Res. Group Treat. Oil Refinery Wastewater, Peking Chem. Works, Peking, Peoples Rep. China). "Use of Ozonation in the Treatment of Wastewater From Oil Refineries". Ch'ing Hua Pei Ta Li Kung Hsuch Pao 2(3):69, 87. Chem. Abstr. 86:47053k.

RE-27* Zaidi, S.A. & F.L. Tollefson, 1976, "Physical-Chemical Treatment of Sour Gas Plant Process Waste Waters". J. Can. Petrol. Technol. 15(2):39-47.

RE-02

Title: "The Purification of [Petroleum Refinery] Waste Waters With Ozone"

Authors: V.A. Alekseeva & Ya.A. Karelin

Source: Neftepererabotka i Neftekhim., Nauchn.-Tekhn.Sb. 5:19-21 (1963)

Soluble petroleum products present in refinery wastewaters are amenable only to treatment by oxidation, e.g., with ozone. An ozonator (PO-3-500) operating at a frequency of 500 Hertz at air pressures of 1.6 to 1.9 atm and producing 1,540 g of ozone/hr, was used in treating a waste containing 20 to 50 mg/l of oil residues, having a BOD of 180 to 259 mg/l and no dissolved oxygen, to produce an effluent containing 2 to 4 mg/l of petroleum residues having a BOD of 8 to 15 mg/l and 1.8 to 2.7% DO.

RE-03

Title: "Ozone Cleans Bug-Ridden Oil."

Author: Anonymous

Source: New Scientist, March, 1973, p. 548.

Describes ozonation for removal of micro-organisms from lubricating oils. Filtration and ozonation at 50 g/hr allowed a French automobile manufacturer to recycle cutting oil and obtain 1 yr of use, whereas oil had been changed previously up to 7 times/yr.

Refers to an earlier Swiss report: Industrial Recovery, 19, #2.

RE-04

Title: "Disposal, Regeneration and Recovery of Used Industrial Oils"

Author: Anonymous

Source: Machine Moderne, p. 38-45, Nov. 1974

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State-of-the-art of the disposal of used industrial oils, and methods for the regeneration and recovery of such oils are described. Some 15% of the used oils collected are regenerated by vacuum distillation for the explusion of volatile hydrocarbons, and hydrolyzed with sulfuric acid with subsequent filtration and adsorption. The recovered oil is processed in a refinery. Some of the used oil collected is incinerated in refineries or in thermal power plants, although most of the used oil is disposed of in sanitary landfills or else in an illegal manner.

According to a new method, cutting oil is regenerated by ozonization at an ozone consumption of 50 g ozone/cu m of oil followed by filter pressing; this permits the recovery of 5% fuel oil. In another process the emulsion is broken by means of ferric chloride and polyelectrolyte. While the supernatant oil can be removed easily, the water containing Fe salts is treated with NaOH for flocculation. Lubricating oils are subjected to ultrafiltration for the quantitative removal of insoluble components, using hexane solvent. If regeneration no longer is possible, the used oil is refined by decantation and filtration to recover fuel oil.

RE-06

Title: "Phenol Free Waste Water"

Author: R.A. Dabine

Source: Chem. Engrg., Aug. 24, 1959, p. 114-117.

Describes the wastewater treatment system at the Cities Service 20,000 bbl/day (now British Petroleum's 80,000 bbl/day) Trafalgar refinery in Bronte, Ontario, Canada. The suggested local discharge standard is 0.015 mg/l for refinery phenols. Biological treatment reduces phenol concentrations from 55 mg/l to 0.38 mg/l, after which ozonation drops this level to 0.012. Addition of 2 mg/l of activated carbon removes the last traces of impurities and brightens the color. Sand filters remove the carbon before discharge to Lake Ontario.

Contactor: A stainless steel vessel, 20 ft high and 15 ft diameter, with perforated carborundum pipes at the vessel base.

Wastewater treatment plant capacity is 300 gpm, but it has handled up to 600 gpm satisfactorily. Total ozone generating capacity is 190 lbs/day, and the 15,000 v generator produces ozone at 8 to 9 kwhr/lb. Cities Service chose ozone over chlorine dioxide because of lower operating costs of ozonation.

RE-07

Title: "Effluent Quality Control At A Large Oil Refinery"

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Authors: D.S. Diehl, R.T. Denbo, M.N. Bhata & W.D. Sitman

Source: J. Water Poll. Control Fed. 43:2254-2270 (1971)

In 1969 a study was conducted at the Baton Rouge Humble Oil Refinery (450,000 bbls/day capacity) to define the refinery's taste and odor contribution to the Mississippi River. The project included discovering the major contributors of odorous wastewater and studying methods of reducing odor in various wastewater streams. As a part of this effort laboratory treatability studies included biological treatment, air stripping, plain detention, activated carbon adsorption and ozonation. The use of ozone was evaluated on 3 wastewaters, and ozone was generally responsible for some reduction in COD and BOD levels.

However, ozone was found to have an unusual effect on the threshold odor of the wastewater streams tested. Whereas oxygenation of the control wastewater caused the threshold odor to decrease continually, ozonation caused the threshold odor to decrease to a certain level and then to increase. In addition, the character of the odor changed from a hydrocarbon odor to a sweet/sour odor similar to that of acetic acid.

No quantitative information is reported concerning the above statement, nor is the method of experimentation discussed. (Abstractors' Note: It is reasonable that acetic acid could accumulate as a reaction product, as it is known to be a stable oxidation product of organic materials and only slowly oxidized by ozone.)

RE-10

Title: "Ozonization of Water Containing Petroleum Products, Aromatic Hydrocarbons, Nitro Compounds, and Chloro-organic Pesticides."

Authors: R.D. Gabovich & I.L. Kurinnoi

Source: Gig. Naselennykh Mest (USSR), Izd. "Zdorov'ya," 31-35 (1967).

Review: Ozonation broke down petroleum product contaminants, aromatic hydrocarbons and nitro compounds. DDT, however, was quite inert to ozone. Chlorination was not an effective method of water treatment for aromatic hydrocarbons, nor for nitro compounds. The compounds tested included the following:

1) Petroleum. About 0.45 mg of ozone was required to break down 1 mg of petroleum at an original concentration of 10 mg/l.

2) Gasoline. 0.023 mg of ozone/mg of gasoline, in 1 min, decreased the [gasoline] from 50 mg/l to 1 mg/l. 5.1 mg/l dosages of ozone fully deodorized the water in 5 min.

3) Benzene. Benzene (200 mg/l) was oxidized and water was fully deodorized by 0.1 mg of ozone/mg of benzene.

4) Diethylbenzene (DEB). 0.7 to 1.0 mg/l of ozone/mg of DEB reduced [DEB] in water from 10-100 to 0.5-0.8 mg/l.

5) α,2,4-dinitrophenol. [DNP] was reduced from 50 mg/l to 0.35 mg/l by doses of 2 mg of ozone/mg of DNP.

6) DDT. At 0.5 mg/l of DDT, 55.2 mg of ozone/mg of DDT were needed to halve the concentration.

Economics: Costs were not analyzed.

References: None

RE-11

Title: "Simulation of a Petroleum Refinery Waste Treatment Process."

Authors: T.W. Hoffman, D.R. Woods, K.L. Murphy & J.D. Norman

Source: J. Water Poll. Control Fed. 45(11):2321-2334 (1973).

Review: The strategy for computer simulation of the steady state operation of the wastewater treatment process at the British Petroleum refinery at Trafalgar, Ontario, Canada is given. Since 1960, this plant has been using physical separation of immiscible oil and particulate matter in API separators and by coagulation, biological removal of dissolved organics by trickling filter and activated sludge, disposal of solids by aerobic digestion, and terminal ozonation to remove trace amounts of dissolved organics (mostly phenols) as well as trace amounts of bacteria and offensive colors, taste and odors. The ozonized effluent is discharged to a lagoon, thence to a lake.

Operational plant data were used to calculate reaction rate constants for the ozonation reactions, assuming zero or first-order kinetics for both a plug flow and continuous stirred tank reactor hypothesis. A first-order reaction combined with a plug flow reactor gave the most consistent results. The [phenol] in the effluent stream can be calculated from the model. The flow rate of air to the ozonator is fixed and the fraction of different components stripped and the fraction of the different components that are oxidized by ozone all are specified.

No specific operational data are given in this paper.

RE-12

Title: "Use of Ozone in Treating Refinery Wastes"

__Authors__: E.G. Ioakimis, A.E. Kulikov, V.I. Nazarov, N.M. Podgoretskaya & S.O. Eigenson

__Source__: Chem. Technol. Fuels Oils 11(3-4):188-192 (1975)

Ozonation was studied in relation to the 3 groups of refinery waste streams, i.e., a mixed waste before biochemical treatment, a contaminated storm-drain effluent, and ELOU [desalter] waste after mechanical treatment. The most effective method of ozonation is multistage contact of the reaction gas with the waste streams. The maximum reduction in contamination (based on COD) is 60%. When the refinery waste streams are ozonated in a counterflow column, the COD and BOD decrease in all stages of the contacting, but the original ratio of BOD/COD hardly changes at all. The first-order linear differential equation chosen was tested in a Minsk-22 computer. Results confirmed the hypothesis of the formation of intermediate products through the interaction of ozone with the initial "contaminant".

__References__: 8

RE-14

__Title__: "Ozone Oxidation of Demulsifiers Present in Waste Waters From Petroleum Refineries and an Evaluation of the Toxicity of the Treated Water"

__Author__: I.I. Malkina

__Source__: Sb.Tr., Mosk. Inzh.-Stroit. Inst. 87:133-6 (1971)

NChK, OP-10 and disolvane-4411 demulsifiers present in concentrations up to 50 mg/l were 92% to 99% oxidized. The ozonized wastes were not toxic to __Daphnia__ __magna__.

RE-15

__Title__: "From Refinery Wastes To Pure Water"

__Authors__: W.T. McPhee & A.R. Smith

__Source__: Engineering Bull., Purdue Univ., Eng. Ext Ser. 109:311-326 (1962)

Describes data obtained after 2 yrs of operation of the full scale, 300 Igpm design flow (600 Igpm peak) wastewater treatment facility installed in 1957 for the 20,000 bbl/day integrated oil refinery of the Cities Service Ltd (now BP) plant on the western shore of Lake Ontario near Bronte in Trafalgar, Canada. Due to the wastewater outfall being relatively near the Bronte water supply intake, the following rigid effluent standards were set as objectives:

Phenolics	less than 20 ppb
Iron	17 mg/l
pH	5.5-10.6
Oil (Total)	15 mg/l
Floating Solids	none
Settlable Solids	none

Ozonation for removal of phenolics (made up of phenols, cresols plus other aromatic fractions) was included as a part of a 10-stage treatment process consisting of:

(1) stripping of sulfides and ammonia,
(2) oil and tank bottoms separation
(3) pH adjustment
(4) temperature adjustment
(5) chemical coagulation and precipitation
(6) 2-stage biological oxidation
(7) final settling
(8) ozonation
(9) adsorption
(10) filtration.

Tests were conducted during the summer of 1960 when the average flow was 225 Igpm. The phenolic design loading was 200 lbs/day at 56 mg/l in the wastewater.

Oil separators operate at removal efficiencies of 85% to 94%. The aerated equalization basin lowers phenolic concentrations from ranges of 40 to 80 mg/l to constant feeds of about 40 mg/l, as well as reducing oil concentrations from 270-400 mg/l to 50-100 mg/l. Flocculator-clarifier units complete oil separation, lowering its concentration below 15 mg/l using 2 g of alum/gal at pH 10.0. This also reduces [COD] from 2,350-1,200 mg/l to 240-440 mg/l and [BOD] from 1,600 mg/l to 160-260 mg/l. Activated sludge treatment (13 hrs) reduced [BOD] from an average of 200 mg/l to approximately 50 mg/l and [COD] from an average of 400 to 150 mg/l. In 10 hrs of activated sludge treatment, phenolic concentrations were reduced from 40 to 1 mg/l or less and, after an additional 3 hrs of aeration and passage through a Dow-Pac filter, to about 0.35 mg/l.

Wastewater streams fed to the ozonation system contained phenolic concentrations of 0.16 to 0.39 mg/l which were oxidized to <0.003 mg/l (3 ppb). Because ozonation treatment meets the established effluent discharge standards, the use of activated carbon has not been necessary since steady state operation of the wastewater treatment plant was attained. Activated carbon was necessary after ozonation during the first 2 months following startup. Rapid sand filtration removed any turbidity that may have been present, and part of the effluent is used in an aquarium (10 ft diameter) containing several species of trout.

The plant effluent is "as good as the raw lake (Ontario) water", except that total solids are higher (1,522 to 1,606 mg/l vs 116 to 224 for raw lake water).

Additional parameters of the final effluent include: ammonia 3.9 to 5.6 mg/l, nitrate 27 mg/l, SS 15 to 32 mg/l, settleable solids 0, DO 4 to 5 mg/l, pH 6.6 to 8.2. The dosages of ozone and reactor dimensions are not given in this article, however some laboratory data developed by the Welsbach Co. on biologically oxidized plant wastewaters are given in Table 10.

TABLE 10. LABORATORY DATA OBTAINED BY OZONATION OF REFINERY WASTEWATER

O_3 Applied, mg/l	O_3 Absorbed, mg/l	Phenol ppb
0	0	800
23	21	30
32	27	16
48	41	11
72	55	13

It is apparent that refinery phenolics are less readily oxidized than is phenol itself. Also, there is an initial rapid destruction of phenolics, followed by a much slower reaction.

Abstractors' Note: This ozonation plant has been operating on full scale since the pilot study was completed in 1960. In a recent review (Ozone Chemistry and Technology: A Review of the Literature 1961-1974, The Franklin Institute Press, 1975) E.W.J. Diaper reports that the reactor is a stainless steel tank 20 ft high and 15 ft in diameter. Ozone is introduced at the tank bottom through diffusers at the rate of 190 lbs/day. At a flow of 300 gpm this would correspond to a dosage of 53 mg/l with a detention time of about 80 min. Diaper reports that the flow varies from 300 to 600 gpm with an ozone dosage in the range of 20 to 40 mg/l.

RE-16

Title: "Ozone Provides an Economical Means for Oxidizing Phenolic Compounds in Coke Oven Wastes"

Author: H.R. Murdock

Source: Indl. & Engrg. Chem. 43(11):125A, 126A, 128A (1951).

Laboratory and pilot studies were conducted on effluents from ammonia stills following Koppers vapor recirculation type dephenolizers, and these studies are detailed in the abstract of this article included under Iron & Steel (I&S-10).

Laboratory studies of treating refining wastes with ozone also are mentioned. Wastewaters containing phenols and sulfides can be treated with ozone, but pretreatment by aeration (to remove sulfides) followed by ozonation (for oxidation of phenols) reduces the ozone demand.

For example, treating refinery wastewater containing 470 mg/l of phenols and sulfides with 1,500 mg/l of ozone reduced the phenols content to zero (at pH 12.0). Aeration of this same waste, followed by pH adjustment to 12.0, then ozonation, required only 1,200 mg/l of ozone to reduce the phenols content to zero.

RE-18

Title: "A Laboratory Study on Ozone Treatment of Refinery Phenolic Wastes"

Authors: M.L. Peppler & G.R.H. Fern

Source: Oil in Canada 11(27):84-90 (1959)

A laboratory study was conducted to determine the feasibility of ozone for treatment of refinery phenolic wastes at Imperial Oil Ltd., Sarnia, Ontario, Canada. One gal samples of waste streams with various pH and interfering substances were placed in a 5 liter cylindrical glass reactor into which ozone was diffused through glass frits at the rate of about 3 g/hr. 150 ml samples were removed over the course of 1.5 hrs.

A Welsbach T-23 lab ozone generator was used. Ozone was prepared in oxygen and determined by the KI method; phenol by the Gibbs method. Off-gases were not analyzed for unreacted ozone.

Results are listed in Table 11.

Ozone demand of an unstripped cat cracker condensate containing 1,450 mg/l S as H_2S, 200 mg/l S as mercaptans and 550 mg/l of phenol was almost negligible until sulfides were oxidized [consuming 1.33 g ozone/g H_2S (estimated from graph)]. Ozone demand of stripped condensate was approximately 5.5 g/g phenol removed. The pH of this sample dropped from 7.4 to 2.3 during ozonation.

An additional test was performed on the effluent from a biological treatment plant: 345 mg/l of ozone was required to reduce the phenol content from 900 to 60 ppb. This corresponds to an ozone consumption of approximately 400 g ozone/g of phenol removed.

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TABLE 11. OZONATION OF REFINERY WASTEWATERS AT SARNIA, ONTARIO, CANADA

Sample	Initial phenol, mg/l	Initial pH	Final pH	g ozone/ g phenol removed
Pure Plant phenol in distd water	492	5.7	2.5	2.4
do.	525	12.3 (buffered)	11.8	1.6
Treating Plant Wash Water	288	9.0	8.9	3.5
do.	296	10.5	9.2	3.5
do.	260	11.7	9.5	4.0
Central Treating Plant Water				
1. Stripped	85	7.9	6.8	4.7
2. Unstripped	114	12.0	7.5	4.0
Cat Cracker Condensate (Stripped)				
1. As is	114	7.0	1.8	6.0
2. pH raised	114	12.6	9.7	6.0

The following comparative costs (1959) are given for alternative methods of phenol removal:

	$/lb of phenol removed
Steam & flue gas stripping	0.91
Biological oxidation (800 lbs/day of phenol)	0.24
Ozone at $0.273/lb ozone & 3.5 to 6 lb ozone/lb phenol	0.95 to 1.65

These conclusions were drawn:

1. Ozone demand of the Sarnia refinery sour waters is in the range of 3.5 to 6 lb of ozone/lb of phenol removed.

2. Stripping is necessary for cat cracker condensates, to remove sulfides which are oxidized prior to phenols.

3. The pH decrease of refinery waste had little or no significant effect (refinery phenolic waste pH normally is in the alkaline range).

4. Easily oxidized substances present in refinery effluent raise the ozone demand.

5. Effluent from the biological oxidation plant had a very high ozone demand. Thus, use of ozone as a polishing agent would not be economically attractive unless a particularly stringent phenol limit was imposed on the effluent.

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RE-20

Title: "Use of Ozone for the Final Treatment of Effluents From An Oil Refinery"

Author: M.A. Popov

Source: Gig. y Sanit. 25(5):92-3 (1960)

A mixture of ozone and air removed 75% to 80% of petroleum products from the wastewater in 16 hrs. Air alone only removed about 60%. The remaining material had little odor, and 4- to 5-fold dilution removed it completely.

RE-22

Title: "Put Ozone To Work Treating Plant Wastewater"

Author: W. S. Sease and G. F. Connell

Source: Plant Engineering, Nov 1966, 2 pages

Briefly discusses the generation of ozone and applications to water, wastewater, and odor control. In discussing waste treatment possibilities, reference is made to the Cities Service (now BP) refinery on Lake Ontario that uses ozone to reduce phenol levels from 300 ppb to 3 ppb in a polishing operation that follows biological oxidation.

Safety aspects are briefly discussed and a toxic exposure limits diagram is included in the Figures.

RE-26

Title: "Use of Ozonation in the Treatment of Wastewater from Oil Refineries"

Authors: Tungfanghung Oil Refinery; Tsinghua Univ.

Source: Ching Hua Pei Ta Li Kung Hsuch Pao 2(3):69,87 (1975)

Wastewater from an oil refinery, after desulfurizing, oil removal, flotation, biological and aeration treatments, can be purified to surface water quality by single or 3-stage ozonization. Good results also are obtained by ozone treatment of the effluent from flotation tanks. This shows the feasibility of replacing the biological treatment by a chemical method.

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RE-27

Title: "Physical-Chemical Treatment of Sour Gas Plant Process Waste Waters"

Authors: S.A. Zaidi & F.L. Tollefson

Source: J. Can. Petrol. Technol 15(2):39-47 (1976)

The feasibility of physical-chemical treatment of sour gas plant wastes was studied on laboratory scale. Experimental data on (a) the adsorption of organic pollutants on Culligan 1627-00 activated carbon, (b) the removal of sulfides from sulfur plant aqueous waste and (c) the chemical clarification of 2 waste streams are presented. Experimental data on the treatment of sour gas plant wastewaters by physical-chemical methods indicate the need for (a) segregation of various waste streams and (b) a combination of incineration, steam stripping, clarification and activated carbon adsorption for the treatment and disposal of different streams. Treatment of the sour gas plant wastewater samples by chlorine-UV oxidation and by ozonation does not appear to be capable of meeting the current waste quality standards.

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LITERATURE CITED (PHARMACEUTICALS) (PC)

PC-01 P.B. Lederman, H.S. Skovronek & P.E. Des Rosiers, 1975, Chem. Engrg. Progress, 71(4):93-97.

PC-02 French Patent 10128W/06. Issued March 21, 1975.

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(4-76)

LITERATURE CITED (PHENOLS) (PH)

PH-01 Bauch, H. & H. Burchard, 1970, "Investigations Concerning the Influence of Ozone on Water With Few Impurities", Wasser, Luft und Betrieb 14(7):270-273.

PH-02* Bauch, H., H. Burchard & H.M. Arsovic, 1970, "Ozone as an Oxidative Disintegrant for Phenols in Aqueous Solutions", Gesundheits-Ingenieur 91(9):258-262.

PH-03 Bernatek, E. & C. Frengen, 1961, "Ozonolysis of Phenols. I. Ozonolysis of Phenol in Ethyl Acetate", Acta Chem. Scand. 15:158-170.

PH-04 Bernatek, E. & A. Vincze, 1962, "Ozonolysis of Phenols. III", Acta Chem. Scand. 16(8):2054-2056.

PH-05 Bernatek, E. & A. Vincze, 1965, "Ozonolysis of Phenols. IV", Acta Chem. Scand., 19(8):2007-2008.

PH-06* Chen, J.W. & G.V. Smith, 1971, "Feasibility Studies of Applications of Catalytic Oxidation in Wastewater", EPA Report 17020 ECI-11/71, 73 pages. U.S. Environmental Protection Agency, Washington, D.C.

PH-07* Chen, J.W., C. Hui, T. Keller & G.V. Smith, 1975, "Catalytic Ozonation in Aqueous Systems", presented at 68th Meeting of Am. Inst. Chem. Engrs., Los Angeles, CA, Nov. (27 pages). Am. Inst. Chem. Engrs., New York, N.Y.

PH-08* Eisenhauer, H.R., 1968, "The Ozonation of Phenolic Wastes", J. Water Poll. Control Fed. 40:1887-1899.

PH-09* Eisenhauer, H.R., 1971a, "Increased Rate and Efficiency of Phenolic Waste Ozonization", J. Water Poll. Control Fed. 43(2):200-208.

PH-10* Eisenhauer, H.R., 1971b, "Dephenolization by Ozonolysis", Water Rsch., 5:467-472.

PH-11 Gabovich, R.D. & I.L. Kurennoi, 1966, "Ozonization of Water Containing Humic Compounds, Phenols, and Pesticides", Vop. Kommunal Gig., 6:11-19.

PH-12 Gilbert, E., 1976, "Ozonolysis of Chlorophenols and Maleic Acid in Aqueous Solution", in *Proc. Sec. Intl. Symp. On Ozone Technol.*, R.G. Rice, P. Pichet & M.-A. Vincent, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 253-261.

PH-13 Gilbert, E., 1978, "Reactions of Ozone With Organic Compounds in Dilute Aqueous Solution: Identification of Their Oxidation Products", in *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*,

TYPING GUIDE SHEET

R.G. Rice & J.A. Cotruvo, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 227-242.

PH-14* Gould, J.P. & W.J. Weber, Jr., 1976, "Oxidation of Phenols by Ozone", J. Water Poll. Control Fed. 48(1):47-60.

PH-15 Hann, V.A. & S.J. Niegowski, 1955, "Treatment of Phenolic Wastes With Ozone", U.S. Patent #2,703,312, March 1.

PH-16 Hirota, D.I., 1970, "Physico-chemical Factors Affecting the Oxidation of Phenolic Compounds by Ozone". Ph.D. Diss., Michigan Univ., Ann Arbor, Mich. Accession #W-73-00170, 162 p.

PH-17* Hillis, R., 1977, "The Treatment of Phenolic Wastes by Ozone", Presented at 3rd Intl. Symp. on Ozone Technology, Paris, France, May. Intl. Ozone Assoc., Cleveland, Ohio.

PH-18 Keay, R.E. & G.A. Hamilton, 1975, "Epoxidation of Alkenes and the Hydroxylation of Phenols by an Intermediate in the Reaction of Ozone with Alkynes". J. Appl. Chem. & Biotechnol., 25(7).

PH-19 Leggett, 1920, U.S. Patent 1,341,913.

PH-20 Loffi, L.E. & E.A. Pedace, 1966, "Residual Liquids Containing Phenols", Saneamiento (Buenos Aires) 30:108-117.

PH-21* Mallevialle, J., 1975, "Action de l'Ozone dans la Dégradation des Composés Phénoliques Simples et Polymerisés: Application aux Matières Humiques Contenues dans l'Eaux". T.S.M.-l'Eau, 70(3):107-113.

PH-22 Marechal, 1905, French Patent 350,679.

PH-23 Nebel, C., R.D. Gottschling, J.L. Holmes & P.C. Unangst, 1976, "Ozone Oxidation of Phenolic Effluents", in *Proc. Sec. Intl. Symp. on Ozone Technology*, R.G. Rice, P. Pichet & M.-A. Vincent, Eds., Intl. Ozone Assoc., Cleveland, Ohio. p. 374-392.

PH-24* Niegowski, S.J., 1953, "Destruction of Phenols by Oxidation with Ozone". Indl. Engrg. Chem. 45(3):632-634.

PH-25 Pasynkiewicz, J. & A. Grossman, 1967, "The Use of Ozone for Eliminating Phenols from Gas Works Effluents", Gas World 166(9):4324.

PH-26* Rosfjord, R.E., R.B. Trattner & P.N. Cheremisinoff, 1976, "Phenols: A Water Pollution Control Assessment". Water & Sewage Works, March, p. 96-99.

PH-27 Sharonova, N.F. & N.A. Kuz'mina, 1968, "Ozonation of Shale Tar Water", Khim. Tekhnol Goryuch Prod. IKH Pererab.

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PH-28* Shuval, H. & M. Peleg, 1975, "Studies on Refractory Organic Matter from Wastewater by Ozonation". Prog. Rpt. to Gesellschaft für Kernforschung, Karlsruhe, Germany and the National Council for R&D, Jerusalem,, Israel, Dec., 23 pp.

PH-29* Smith, G.V., J.W. Chen & K. Seyffarth, 1972, "Catalytic Oxidations of Aqueous Phenol", Proc. Fifth Intl. Congress on Catalysis, August, p. 893-903.

PH-30 Spanggord, R.J. & V.J. McClurg, 1978, "Ozone Methods and Ozone Chemistry of Selected Organics in Water I. Basic Chemistry", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors, Intl. Ozone Assoc., Cleveland, Ohio, p. 115-125.

PH-31 Throop, W.M., 1975, "Perplexing Phenols. Alternative Methods for Removal". Proc. Third Annual Pollution Control Conference, WWEMA, p. 115-143. Water & Wastewater Equipment Mfgrs. Assoc., McLean, VA.

PH-32* Throop, W.M., 1977, "Alternative Methods of Phenol Wastewater Control", J. Hazardous Materials 1:319-329.

PH-02

Title: Ozone as an Oxidative Disintegrant for Phenols in Aqueous Solutions

Authors: H. Bauch, H. Burchard, & H. M. Arsovic

Source: Gesundheit-Ingenieur 91(9):258-262 (1970)

Review: Outlines laboratory reactions at 22°C and describes products of ozonation of the following compounds: phenol; ortho-, meta- and para-cresols; 5 xylenols; chlorobenzene; various chlorophenols and chlorocresols; other phenols; naphthols and phenols with more than 1 OH group.

Two reactions probably take place; both involving ring splitting: (1) via the ozonide yielding smaller molecules and (2) via direct oxidation (ozone decomposition, free oxygen) yielding larger end products. The former is the initial reaction. Products found include: glyoxylic acid, propionic acid, maleic acid, mesotartaric acid, glycolic acid, oxalic acid and carbon dioxide. Treatment of chlorinated phenols produced HCl. Off-gases were hydrocarbon-free. In general, more highly substituted compounds were more reactive, especially if the OH groups were sterically unhindered. Oxidizable decomposition products increased consumption of ozone. Compounds were found to be 70% to 80% decomposed after application of 2 to 3 moles ozone/mole of reactant; doubling ozone dosage brought decomposition to 100%. Decomposition products were biologically non-toxic after sufficiently long ozone treatment.

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Ozone Generator: Supplied by Gesellschaft für Ozontechnik und Anwendung and used a synthetic gas mixt of 21% oxygen and 79% nitrogen (to exclude influence of air pollutants).

Ozone contactor: A 2-stage reactor with a 80 mm high lower stage and an upper stage 200 mm high filled with Raschig rings. The upper stage was unnecessary in most cases due to the readily reacting nature of phenols. Ozone was fed in via a glass tube (35 mm diam x 700 mm). Ozone content was determined iodometrically. All reactions were followed by gas chromatography. In no cases were volatile hydrocarbons found.

Phenol can be decomposed by ozone at room temperature to the extent that it cannot be detected either by gas chromatography or by p-nitroaniline. Acids are formed during ozonation which are non-ring-containing, aliphatic acids and the molecules are always smaller than the phenol molecule. Initial phenol decomposition takes place almost exclusively via the ozonide, resulting in monobasic acids. With increasing reaction time, other aromatic ring scission products (polybasic acids) are formed. Phenol decomposition is 70% complete at 3 moles ozone/mole of phenol, and is 100% complete at 5.5 moles (200 g ozone/100 g phenol).

Cresols are decomposed significantly more easily than phenol. m-Cresol decomposes more easily than o- or p-cresols, and the reaction takes place significantly more rapidly in acid medium than in basic (80% decomposition at 2 moles of ozone/mole of cresol -- 85 g of ozone/100 g of cresol). Ozonation of cresols produces glyoxylic acid, glyoxal and keto-aldehydes. At first, the methyl group is oxidized, forming hydroxybenzoic acids (salicylic acid has been identified upon ozonation of o-cresol), which oxidize further to aliphatic mono- and dibasic acids [(maleic acid (I)], mesotartaric acid by further oxidation of I, acetic acid, propionic acid, glycolic acid, glyoxylic acid, oxalic acid) and CO_2. All 3 cresols (o-, m- and p-) produced the same products upon ozonation -- only the reaction rates differed. Complete oxidation takes place with 4 moles of ozone/mole of cresol.

Xylenols with OH groups ortho or para to the methyl groups react fastest with ozone, and all react faster than the cresols to produce the same oxidation products as do the cresols. In addition, diacetyl is formed from 1,2,3- and 1,2,4-xylenols. Glyoxal is also formed, which disproportionates to glycolic acid in alkaline medium. Keto-aldehydes and hydroxyphthalic acid also form, which oxidize further. Xylenol ozonation takes place more rapidly in acid medium, about 80% being decomposed at an ozone/xylenol ratio of 2/1.

Ozonation of chlorobenzene is slower than phenols, probably because of its lower solubility, but it forms the same decomposition products as phenol, plus HCl, chlorotartaric acid, o-, m- and p-chlorophenols. Chlorocresols and chlorophenols behave similarly upon ozonation. Naphthols, thiophenols and phenols with several OH groups decomposed by ring rupture as well.

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The authors conclude that phenolic decomposition takes place initially via the ozonide, 3 moles of ozone being consumed/mole of phenol, and forming 3 moles of H_2O_2. Phenolic oxidation products, in turn, consume ozone. Direct oxidation also occurs via the oxygen liberated by ozone decomposition.

Economics: Not mentioned

PH-06

Title: "Feasibility Studies of Applications of Catalytic Oxidation in Wastewater."

Authors: J.W. Chen & G.V. Smith

Source: EPA Report 17020 ECI-11/71 (1971), 73 pages. U.S. EPA, Washington, D.C.

Review: Outlines the application of sonocatalysis to advanced wastewater treatment. In addition to sonocatalytic oxidation, sonocatalytic ozonation and catalytic ozonation using Raney Ni catalyst each were tested on treatment plant effluent, on aqueous solutions of phenol and of o-chloronitrobenzene (OCNB).

Apparatus: Welsbach T23 (68 mg ozone/hr at 1.15 mg/l) and Welsbach T408 (10 g ozone/hr at 33 mg/l) ozone generators. The ozone reactor was a Pyrex tube, 2.25 x 16 inches, with 2 2-mm ID glass tubes for sparging gas at the bottom.. Sonics were applied by an 880 KHz macrosonic submersible piezoceramic transducer with 1.5 sq in surface area mounted at the center of the bottom of the constant temperature jacket. A macrosonics 180-VF high frequency generator supplied power to the transducer.

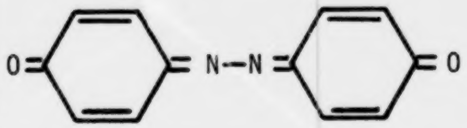
Raney Ni Catalyst: was stirred magnetically in the reaction mixture.

Results: Wastewaters from the Carbondale, Illinois sewage treatment plant (350 ml samples) showed 78% decrease in COD and 96% decrease in ODI (Oxygen Demand Index) after 2 hrs insonation in the presence of activated Raney Ni catalyst. At 800 Hz the fastest removal occurred at 18.2 watts/sq cm. Sono-ozonation (68 mg/hr of ozone - 33.3 watts/sq cm) for 2 hrs reduced [COD] by 75%. Raney Ni catalyzed ozonation (10 g/hr ozone, 14,300 mg/l Raney Ni, without sonics) removed 85% of COD and 60% of TOC in 2 hrs. Stirring of the Ni catalyst was required.

Aqueous solutions of phenol (500 mg/l - 200 ml samples) were treated 3 hrs and samples withdrawn every 0.5 hr. Ozonation alone (65 mg/hr) decreased [phenol] 31% in 3 hrs. Ultrasonics alone caused a 60% decrease in [phenol], almost linearly. This decrease was unaffected by addition of 160 g of Raney Ni. Combined sono-ozonation decreased [phenol] 91%, and addition of 160 g of Raney Ni decreased [phenol] by 95%. Excess Raney Ni was less effective. Of the ozone fed into the reaction system, 40% was consumed during catalytic ozonation and 75% during sonocatalytic ozonation.

Compounds identified by UV and TLC from oxidation of phenol were: catechol, hydroquinone, quinone and pyrogallol. Oxidation times were 0.25 to 3.5 hrs. With either ozonation or Raney Ni catalyzed ozonation, some hydroquinone and catechol were left in solution. However, in solutions treated 6 hrs by sonocatalytic ozonation, those intermediates disappeared.

Saturated OCNB solutions in 200 ml distilled water (0.002M) and 2 g Al powder or 2 g activated Raney Ni (solid OCNB present in all runs) were irradiated with ultrasound at 800 KHz and sparged 24 hrs with ozone/oxygen. All OCNB and its ozonation products were destroyed. In 6-hr experiments using insonation alone, 3 intermediate oxidation products were formed, isolated and tentatively identified as 2,2'-dichloroazoxybenzene, o-chlorophenyl-hydroxylamine and:



Economics: None mentioned.

References: 21

PH-07

Title: "Catalytic Ozonation in Aqueous Systems"

Authors: J.W. Chen, C. Hui, T. Keller & G.V. Smith

Source: Presented at 68th Mtg. of Am. Inst. Chem. Engrs., Los Angeles, Calif., November, 1975, 27 pp. Am. Inst. Chem. Engrs., New York, N.Y.

Review: Investigation of catalytic ozonation (using a special Fe_2O_3 catalyst) compared the efficiency with results from ozonation and catalytic oxidation. Substances oxidized were phenol, ethyl acetoacetate, and an industrial waste from a chemical company. Variables were gas flow rate, [ozone], liquid retention time and feed concentration.

Comment: Catalytic ozonation allows at least 2 oxygen atoms from each ozone molecule to be utilized in the oxidation reaction with phenol. Steady state was reached in 90 min using ozone alone and in 60 min using catalytic ozonation. At initial [COD] up to 900 mg/l, 100% removal of COD was obtained by catalytic ozonation, whereas in the same contact time only 65% (at 200 mg/l initial COD) and 30% (at 900 mg/l initial COD) of the initial COD was removed by ozonation alone (0.2 l/min; 30 mg/l [ozone]. Increased contact times produced increased removal efficiencies, and also could be correlated to [ozone] in the feed gas.

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Ethyl acetoacetate is only slowly oxidized by ozone alone (<10% reduction in [COD] in 2 hrs). With catalytic ozonation, however, 40% of the COD was removed in 2 hrs.

Ozone Generator: The ozone generator was not mentioned.

Contactor: A packed bed reactor (glass beads) was used for the steady state continuous operation, and at least 12 liquid retention times were employed as contact times (25 min). The flow rate of oxygen or ozone was 0.1 to 0.2 l/min, and [ozone] was 16 to 30 mg/l.

Economics: No specific costs were given, however, the authors maintain that this process makes ozonation economically feasible.

PH-08

Title: "The Ozonation of Phenolic Wastes."

Author: H.R. Eisenhauer

Source: J. Water Poll. Control Fed. 40:1887-1899 (1968)

Subject: A laboratory study of the oxidation of dilute solutions of pure phenol. Information is generated on reaction rates, flow rates of ozone, oxidation products of phenol and their reaction kinetics.

Equipment: Welsbach T-816 Ozonator, Welsbach PA-1 Dryer, Welsbach H-81 Ozone meter, No. 448-118, Lab-crest flowmeter tube, Beckman KD-ZA Spectrophotometer. The contactor was a sintered dispersion tube in a 38 cm tall cylinder, 70 mm OD.

Ozone Adsorption: Ozone content in the gas lines before and after reaction was measured by reaction with potassium iodide and titrated with sodium thiosulfate.

Major Conclusions:

The rate of phenol degradation may be increased by:

(1) Increasing [ozone] in the feed stream
(2) Increasing gas flow rate
(3) Reducing gas bubble frequency
(4) Increasing bubble frequency
(5) Increasing gas-liquid contact time.

The first phenol oxidation product was assumed to be catechol, but hydroquinone also was found. After consumption of about 4 moles of ozone, substantially all the phenol originally present had disappeared.

During the reaction time cited (up to 1 hr), very little phenol was oxidized completely to CO_2 + water. The above parameters also were found to have little effect on reaction efficiency.

Calculations of ozone feed, unreacted ozone, effect of flow rate, and catechol formation and degradation are contained in 3 appendices.

Cost data: none cited

References: 13

PH-09

Title: "Increased Rate and Efficiency of Phenolic Waste Ozonization.

Author: H. R. Eisenhauer

Source: J. Water Poll. Control Fed. 43(2):200-208 (1971a)

Dilute solutions of pure phenol were used in the experimental procedure, and oxidized with ozone to produce its sequential oxidation products:

Phenol → Catechol → o-Quinone → yet to be identified → $CO_2 + H_2O$

Equipment: Welsbach T-816, Welsbach PA-1 Dryer, Beckman Carbon Analyzer.

Contactor: Porous frit in cylinder 70 mm diameter and 38 cm long.

Results: [Phenol] of 50 to 300 mg/l were ozonized at initial pH values of 3 to 9 and reaction temperatures of 20° to 50°C. The rate of ozone consumption up to 15 moles/mole of phenol was constant at about 57% of the ozone feed. Then at about 22 moles/mole of phenol, all the ozone supplied to the reaction mixture was consumed. The rate of phenol degradation in unbuffered solution was virtually unaffected by pH, except at pH 11, at which the rate doubled.

As the reaction proceeded, the TOC of the solution decreased, but no CO_2 formed until about 1.5 moles of ozone had been consumed, presumably reflecting conversion of phenol to its first oxidation product, catechol. CO_2 formation then began at a rate directly proportional to the ozone consumption. When about 33% of the theoretical amount of the CO_2 had been formed, CO_2 production ceased. Some mechanism of ozone decomposition became operative, presumably being catalyzed by a phenol oxidation product.

At 50°C, initial reaction efficiency increased to about 65%, and a greater proportion of phenol was oxidized to CO_2. At 15 moles of ozone/mole of phenol at 50°C, CO_2 production continued, but at a much reduced rate.

If the mechanism of phenol ozonization were free radical or involved the intermediate formation of H_2O_2, ferrous salts might be expected to catalyze the reaction. Instead, ferrous salts inhibited the ozonization. The pH dependence of initial phenol oxidation suggests that the reaction is ionic.

Conclusions:

(1) Economical ozonation of phenol to CO_2 and water is not feasible.
(2) The initial efficiency advantage gained at pH 11 was lost as primary oxidation products were produced.
(3) If the first stage of oxidation is sufficient to satisfy a pollution control problem, 98% of the phenol can be removed using 5 moles of ozone/mole of phenol.

Cost Factors:

At an ozone cost of \$0.07/lb (\$0.15/kg), a treatment cost of \$0.18/lb of phenol (\$0.40/kg) is calculated (98% removal).

References: 5

PH-10

Title: "Dephenolization by Ozonolysis"

Author: H.R. Eisenhauer

Source: Water Research 5:467-472 (1971b)

Laboratory studies were conducted on solutions of phenol in water.

Contactor: Ozone (in air) was passed through a sintered glass dispersion tube (70 mm diameter x 38 cm high) charged with 1,000 ml of phenol solution. The gas stream entering and leaving the reactor was analyzed iodometrically for ozone. Residual phenol in solution was followed by UV absorption. Initial [phenol] was 50 to 300 mg/l, [ozone] in the gas stream was 15 to 30 mg/l and ozone flow rates were 0.2 to 0.5 l/min.

Results: Phenol degradation efficiency increased with ozone dose rate and contact time, and decreased with ozone gas bubble diameter.

Ozonation of neutral, unbuffered, dilute phenol solutions reduced the pH to 3 to 3.5 rapidly. When the initial pH was adjusted to 3 to 9, the rate of phenol degradation did not change. At an initial pH of 11, the reaction rate more than doubled and the system remained basic.

No significant effect of temperature was observed (20° to 50°C) on the rate of phenol ozonation, but increasing temperature did increase the rate of complete oxidation to CO_2. Oxygen added to the ozonized air had no effect upon the reaction rate. Both ferrous sulfate and ferrous ammonium

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sulfate inhibited the ozonation of phenol, indicating that the mechanism is not free radical and/or does not involve the intermediate formation of H_2O_2.

During exhaustive ozonation of phenol at 20°C, no CO_2 was formed until 1.5 moles of ozone had been consumed, presumably reflecting conversion to its first oxidation product, catechol. CO_2 formation then began at a rate directly proportional to the ozone consumption, 1 mole of CO_2 being formed for each 7.3 moles of ozone consumed. Since 2.33 moles of ozone theoretically should produce 1 mole of CO_2, the reaction efficiency was only 30%.

After about 33% of the theoretical amount of CO_2 had formed, the ratio of CO_2 formed/ozone consumed changed dramatically and CO_2 production ceased.

At 50°C, the initial reaction efficiency increased to about 65%, a greater proportion was converted to CO_2 (less than double) and formation of CO_2 continued with continued addition of ozone.

Conclusions: Complete oxidation of phenolic effluents cannot be achieved economically with ozone alone. The initial efficiency advantage gained at pH 11 disappears as soon as most of the phenol has been oxidized to the primary oxidation products. If this 1st stage of oxidation is sufficient to satisfy a pollution control problem, then 98% of the phenol can be "destroyed" using only 5 moles of ozone/mole of phenol. At an ozone cost of 7¢/lb, this is equivalent to a treatment cost of 18¢/lb of phenol destroyed.

PH-14

Title: "Oxidation of Phenols by Ozone."

Authors: J.P. Gould & W.J. Weber, Jr.

Source: J. Water Poll. Control Fed. 48(1):47-60 (1976)

Study: Describes a laboratory study of the oxidation of phenol by ozonolysis and delves heavily into the organic chemistry involved. Reactions of ozone with phenol were investigated to determine (a) the rate at which phenol is destroyed by ozone and (b) the specific products of ozonolysis of phenol and their behavior under continued application of ozone.

Equipment: Welsbach T-23 Ozonator plus a 500 ml cylinder fitted with coarse porosity sintered glass plate diffusers. [Ozone] was followed by the KI procedure and gas flow rates were monitored. [Phenol] ranged from 1.4 to 1,106 mmoles/l in phosphate buffered solution. Ozone dose rates were 0.774 to 8.076 moles/mole of phenol originally present.

Results: The rate constant (K_a) for overall disappearance of phenol (I) from aqueous solutions is 0.132 mole of phenol/mole of ozone. Over a pH range from 2.27 to 11.06, K_a ranged from 0.11 at low pH to 0.28 at high pH. Most of this increase in K_a occurred between 4 and 7.5, and was essentially

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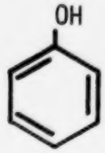
complete by pH 8. The bulk of change in K_a is completed long before a significant degree of ionization of I has taken place.

During the early stages of ozonation of I, hydroquinone (II) is present at all times in substantially higher concentrations than is catechol (III). The combined total concentration of II and III reaches a maximum level only slightly above 10% of the initial concentration of I, indicating that hydroxylation of I is not the most important mode of action of ozone in this system. The concentrations of II and III pass through maxima during the first 5 minutes of reaction, then fall to relatively insignificant levels in about 10 minutes.



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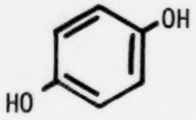
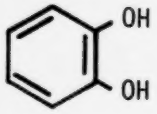


hydroquinone(II)

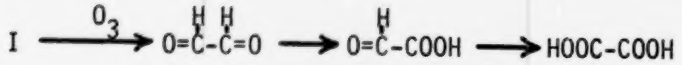


catechol (III)

Glyoxal (IV) and glyoxylic acid (V) account for the bulk of the organic carbon present in the reaction mixtures throughout the greater part of the ozonization runs. [IV] increases to a maximum in the first 10 minutes, followed by a smooth and gradual dropoff thereafter, reaching very low values after 30 minutes. At its maximum concentrations, IV accounts for over 25% of the TOC. Since this level is higher than that of II plus III, ring cleavage is much preferred to hydroxylation.

[V] passes through a 1st peak after 5 minutes of ozonation (well before the IV peak) and through a 2nd peak at about 18 minutes (well after the IV maximum). Thus it is likely that V arises from both ring cleavage of I and oxidation of IV. V accounts for virtually all organic carbon in the mixtures after 20 minutes of ozonation.

[Oxalic acid] (VI) rises very slowly, reaching 3% of the organic carbon originally present after 30 minutes of ozonization. This indicates that V forms water and CO_2 without passing through VI.



$$\mathrm{I} \xrightarrow{O_3} \mathrm{O{=}\overset{H}{C}{-}\overset{H}{C}{=}O} \longrightarrow \mathrm{O{=}\overset{H}{C}{-}COOH} \longrightarrow \mathrm{HOOC{-}COOH}$$

glyoxal (IV) glyoxylic acid (V) oxalic acid (VI)

In the systems studied, addition of 24 moles of ozone/mole of I lowered [COD] 77%. To lower [COD] by another 3% required 24 additional moles of ozone/mole of I, and to attain 90% COD reduction would require >150 moles of ozone/mole of I. Thus ozonation beyond the aromatic ring breakpoint is uneconomical. However, IV and V are relatively inoffensive and readily biodegradable in comparison with I. Thus, a ratio of 4 to 6 moles of ozone/-mole of I originally present will assure virtually complete removal of I and its aromatic by-products. At this point about 33% of the initial organic carbon will remain, being about evenly divided between IV and V, and a 70% to 80% reduction in [COD] will have been achieved. [VI] will be <0.5 mg/l. The aromatic breakpoint may be used as an indicator of optimum ozone dosage. This can be followed with a COD or TOC monitor.

PH-17

Title: "The Treatment of Phenolic Wastes by Ozone"

Author: R. Hillis

Source: Presented at 3rd Intl. Symp. on Ozone Technology, Paris, France, May, 1977. Intl. Ozone Assoc., Cleveland, Ohio.

Ozonation of 14 phenols in water was studied over a pH range of 4.0 to 10.0. Ozone was prepared from oxygen, usually at 3.5 g/hr at concentrations of 22 to 27 g/cu m. Three liters of phenol solution (30 mg/l in water) were ozonized in a 1 m tall, 80 mm diameter glass tube, using a sintered glass disc. The amounts of ozone in feeds and in off-gases were determined to calculate the amount of ozone consumed. Phenols were analyzed before and after ozonation (Table 12).

After 10 minutes, [I] was 1.18 mg/l. UV spectrophotometry showed that as I was being destroyed, another compound (unidentified) was being formed; this unidentified compound was itself destroyed upon continued ozonation.

Destruction of II and III was faster at higher pH during the initial period of reaction; however this pH effect became less important as [phenols] became lower.

CODs of solutions of 6 phenols were studied before and after ozonation (Table 13).

TABLE 13. EFFECTS OF OZONATION OF PHENOLS ON SOLUTION CODs

Phenol	Time of ozone treatment (mins)	COD at start (mg/l)	COD at finish (mg/l)
Phenol	8	70	24
Phenolsulphonic acid	8	29	11
Hydroquinone	8	58	18
Pyrogallol	8	33	14
Pentachlorophenol	20	89	44
β-Naphthol	30	26	19

TABLE 12. OZONATION OF PHENOLS

Phenol	Flow of Ozonized Oxygen	[Ozone] (mg/1)	Treatment Time (minutes)	Residual Phenol (mg/1 as Phenol)	g Ozone/g Phenol (as phenol except where noted) to reduce 30 mg/1 of phenol to <0.5 mg/1
Phenol (II)	2.9	27.59	8	0.10	2.5
Phenolsulfonic Acid (III)	2.9	27.59	8	0.10	2.7
Hydroquinone	2.35	23.91	12	0.13	3.0
Pyrogallol	2.35	21.36	8	0.20	2.0
p-Chlorophenol	2.35	22.26	10	N.D.	2.5
Pentachlorophenol (I)	2.35	24.48	35	0.38	3.8
m-Aminophenol	2.35	25.96	6	0.01	2.2
p-Nitrophenol	2.35	25.02	10	0.05	2.5
o-Cresol	2.35	24.98	8	0.10	2.5
m-Cresol	2.35	24.29	10	0.05	2.5
p-Cresol	2.35	26.02	8	0.5	2.3
2,6-Xylenol	2.35	27.09	6	N.D.	1.9
β-Naphthol	2.35	27.06	4	0.10(a)	4.2(a)
Dichlorophen	2.35	22.76	10	0.05(b)	2.5(b)

N.D. None detected
(a) Analyzed as β-naphthol
(b) Analyzed as dichlorophen

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In the 1st 4 cases, the COD was destroyed steadily, but in the last 2 cases there was an initial rise in COD during the 1st few minutes, followed by a steady reduction in COD value.

At higher [ozone] (22 g/cu m), the rate of phenol oxidation was much faster than at lower concentrations (4.9 g/cu m). Furthermore, the ozonation time required to attain lower phenol levels also decreased with increasing [ozone].

Under these treatment conditions, 10 minutes ozonation time reduced [phenol] from 30 mg/l to <0.5 (in many cases <0.1) mg/l, except for I. The g of ozone consumed/g of phenol was 2.0 to 3.0, or 4 to 6 moles of ozone/mole of phenol. COD values were lowered 50% to 67%, but were not eliminated by these ozone dosages, indicating that organic compounds remained after ozonation.

Oxidation products of these phenols were not identified.

For effluent treatment purposes, pH adjustment (to 8.5 to 10) would be justified only if residual [phenol] of 1 mg/l is desired.

The effect of pH upon ozonation times was determined for I and III (Table 14).

TABLE 14. EFFECT OF pH ON OZONATION OF A 30 MG/L SOLUTION OF PHENOL

pH	Time (mins) to reduce phenol concentration to		
	5 mg/l	1 mg/l	less than 0.1 mg/l
4.0	4.0	5.7	∿8.0
7.0	3.6	5.4	∿8.0
8.5	2.5	4.7	∿8.0
10.0	1.2	2.8	∿8.0

When considering ozonation of coke oven effluents from the Iron and Steel industry, for example, ozone will destroy thiocyanates (which are oxidized to cyanide, then to cyanate, which hydrolyzes to carbonate and ammonium ions). Thus total ozone demand of such a waste will depend upon concentrations both of phenols and thiocyanate compounds. Ozonation should be a good polishing step for effluents which have received primary treatment by other methods.

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PH-21

Title: "Action of Ozone in the Degradation of Simple and Polymeric Phenolic Compounds. Application to Humic Materials Contained in Waters".

Author: J. Mallevialle

Source: T.S.M. l'Eau 70(3):107-113 (1975)

Review: Ozonation of phenol (I), salicylic acid (II) and humic acids (III) was studied. The contact chamber (2.5 l volume) was 65 x 750 mm, operated as a closed system, with ozone in oxygen fed at an average rate of 30 l/hr. Homogenization of gas and liquid was effected by means of a peristaltic pump at the base of the column.

Relatively concentrated solutions were used (100 to 200 mg/l) and gas dosages of 1.1 l/min, containing 25 mg/l of ozone. Absorption at 210, 270 and 420 nm, [phenol] and total acidity were measured.

Ozonation of I produced catechol and o-quinone (as expected by the mechanisms of Eisenhauer), but also hydroquinone and p-benzoquinone. These results confirm the mechanism proposed by Eisenhauer: electrophilic attack of ozone at the ortho and para positions in I.

In ozonation of II, the TOC value remained constant during the 1st 10 minutes, but degradation of II proceeded faster than degradation of I. Phenol, catechol and 3 other still unidentified phenolic compounds were isolated, and 2,3-dihydroxybenzoic acid was shown to be absent. A little more than 3 moles of ozone were required to degrade 1 mole of II, at which point no traces of II could be detected by infrared absorption. Strong absorptions for OH and COOH were observed, indicating that a mixture of carboxylic acids had been formed. Ozonation of II was shown to be first-order for reduction of TOC and TOD values.

Natural waters containing 100 to 200 mg/l of III were ozonized. Color decreased rapidly (90% reduced in 10 min), corresponding to a rapid depolymerization. After 20 minutes, a violet color appeared, due to oxidation of decomplexed Mn. Chromatographic studies showed the presence of phenolic compounds as intermediates, but these were not identified. The presence of formic acid was indicated. These results might also be obtained by ozonizing synthetic solutions of pesticides and phthalates complexed by humic acids. In effect, it is possible to increase the concentrations of these complex compounds by insufficient ozonation.

The authors conclude that for treatment of drinking waters containing phenolic materials, one must be careful to use a minimum quantity of ozone. I and salicylic acid initially form other phenolic derivatives upon ozonation, and these new derivatives require a new and equally large dose of ozone to degrade them. Waters containing 525 mg of humic acids require 100 mg of

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ozone to destroy 95% of the color and 320 mg to destroy 95% of the polyhydroxyaromatic derivatives. Thus it is necessary to add 380 and 500 mg of ozone to lower 75% of the COD and TOC values, respectively.

Therefore, if ozone is used as a water sterilant, one must consider that phenolic intermediate oxidation products will be formed unless a sufficient amount of ozone is added to degrade these as well. When ozone is used as the last stage of a water treatment process, the contact time should not be decreased below that required for virucidal or bactericidal action (0.4 mg/l -- 6 min). One can also use more efficient contacting systems or follow ozonation with activated carbon filtration.

PH-24

Title: "Destruction of Phenols by Oxidation with Ozone."

Author: S.J. Niegowski

Source: Industrial & Engineering Chemistry, 45(3):632-634 (1953)

Experimental: 500 ml samples were ozonized in a gas washing bottle. Ozone concentrations 1% to 2% ozone by weight were used, generated by a Welsbach T-23 generator. A 2nd gas washing bottle was used to collect excess ozone in a 2% KI solution to determine the relative amount of ozone that had passed through the sample.

Results: Solutions of 100 mg/l of phenol and distilled water were adjusted to pH 12 and ozonized (Table 15).

Solutions of various phenolic wastes were oxidized to 99% removal (Table 16).

pH Effect: Elevated pH (about 11.8) tended to favor phenol removal.

Oxidation of thiocyanate: 3 parts of ozone were required to oxidize 1 part of SCN^- to CN^-.

Effect of Sulfide: Prior aeration to remove sulfides reduced the ozone demand during phenol oxidationn.

Reduction of COD and Color Levels: Oxidation of 1,000 mg/l of pure phenol in water at pH 12 is presented in graphic form.

Toxicity of Oxidation Products: An initial [phenol] of 200 mg/l was ozonized to 0.1 mg/l. Safe phenol dosage for exposure of blue gills, diatoms and mayfly larvae was found to be 2.1 mg/l. The ozonated phenol solution had no toxic effects on any of the organisms tested.

Cost Information: none cited.

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TABLE 15. OZONATION OF PHENOL, o-CRESOL AND p-CRESOL

Phenol		o-Cresol		m-Cresol	
Ozone dosage (mg/l)	Phenol remaining, (mg/l)	Ozone dosage (mg/l)	o-Cresol remaining, (mg/l)	Ozone dosage, (mg/l)	m-Cresol remaining, (mg/l))
0	96	0	99	0	99
54	47	49	49	57	41
110	12	100	11	110	2.7
180	0.4	150	1.7	150	0.4
220	0.2	200	0.2	200	0.0
260	0.1	240	0.1	260	0.0

TABLE 16. OZONATION OF PHENOLIC WASTES TO 99% REMOVAL

Source	Initial Phenols (mg/l)	Ozone Demand (mg/l)	Ozone/ Phenol (mg/l)	Residual Phenols (mg/l)
Coke plant A	1,240	2,500	2.0	1.2
Coke plant B	800	1,200	1.5	0.6
Coke plant C	330	1,700	5.2	1.0
Coke plant D	140	950	6.8	0.1
Coke plant E	127	550	4.3	0.2
Coke plant F	102	900	8.8	0.0
Coke plant G	51	1,000	20.0	0.4
Coke plant H	38	700	18.0	0.1
Chemical plant*	290	400	1.4	0.3
Refinery A	605	750	1.3	0.3
Refinery B	11,600	11,000	1.0	2.5

* This waste contained 2,4-dichlorophenol. Results are expressed as 2,4-dichlorophenol.

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Title: "Phenols: A Water Pollution Control Assessment."

Authors: R.E. Rosfjord, R.B. Trattner, & P.N. Cheremisinoff.

Source: Water & Sewage Works, March 1976, 96-99

Review: A comprehensive review of the known methods of treating phenolic wastes. Ozone is mentioned briefly and labelled as uneconomical.

Cost Equation: One reference cited lists ozone operating cost as \$0.75/lb of phenol removed. Operating costs and capital depreciation are computed via the following equation:

$$0 = (330)QXP + (90{,}000)(F/100)0.6F > 20$$

and

$$0 = 330QXP + (350{,}000)F < 20$$

Q = daily phenol rate (lbs of phenol/day)
X = ozone requirement (2 lbs of ozone/lb of phenol)
P = price of ozone (\$0.25/lb) (includes capital cost)
F = flow rate (gal/min)

References: 74 (only 4 dealing with ozone, and none of these are primary references).

Abstractor's Comment: An incomplete review of the published literature on ozone treatment of phenolics.

PH-28

Title: "Studies on Refractory Organic Matter from Wastewater by Ozonization."

Authors: H. Shuval & M. Peleg

Source: Prog. Rept. to Gesellschaft für Kernforschung, Karlsruhe, Federal Republic of Germany and the National Council for R&D, Jerusalem, Israel, Dec. 1975, 23 pp.

Review: A progress report of the study of ozonation of organic compounds, as measured by COD; emphasis was placed on the effect of the pH level. Synthetic solutions of phenol, chlorophenol and wastewater effluents from municipal sources and from a high rate oxidation pond were ozonized to study the effects of the following parameters on ozonation at different pH values: TOC, nitrogen-containing compounds, ether extractibles, carbohydrates,

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tannins, proteins, fulvic acid, humic acid, hymethomelanic acid, carboxylic acids and organochloro compounds. Mention is made of virus destruction, which is somewhat hindered due to the clumping action of viruses.

The reaction rate of ozone with chlorophenol was markedly influenced by the solution pH, being faster at a basic pH than at an acidic pH. Starting at pH 10, the reaction was more rapid when the pH was maintained at 10 than when it was not controlled. Where the pH was allowed to decrease, it reached a value of about 2.5, at which stage the reaction could not be followed at a measurable rate. At the same pH, almost the same reaction rate was obtained in the ozonation of both phenol and o-chlorophenol. When the oxygen flow rate was varied from 20 l/hr to 40 l/hr (ozone supply of 4.3 and 7.3 mmoles/20 min., resp.), the reactions were propagated at almost the same rate. The rate of CO_2 formation increased with increasing pH. 80% of the organic chlorine from o-chlorophenol was converted into chloride ion; the formation of chloride ion continued even after all the o-chlorophenol had reacted. Although chlorophenol was destroyed upon ozonation (40 min), total carbon remained nearly constant at pH 8 and decreased by about 30% at pH 4. Organic oxidation products were not isolated and identified.

For both types of actual wastewaters, the primary decrease in organic pollution occurred in the 1st hr of ozonation, after which it proceeded at a very slow rate. About 3 g/hr of ozone was needed to oxidize the carbon and nitrogen compounds to CO_2 and nitrate, resp. Doubling of the oxygen flow rate from 20 to 40 l/hr did not significantly affect the kinetics of the degradation of chlorophenols; the steady state [ozone], rather than the flow, seemed to affect the ozonation reaction rates. The dissolved [ozone] seemed to be related to pH changes, decreasing after the maximum concentration had been reached, as the pH increased. At the same time the organic content decreased, thus decreasing the ozone demand of the pollutants. Nitrogen was oxidized finally to nitrate in both types of wastewater.

Ozone Generation: A flow rate of 40 l/hr of dry oxygen was used to produce 20 mg/min of ozone. The applied amperage was 200 to 215 ma.

Contacting: Two ozonation techniques were used. In the 1st, ozone was bubbled through the test soln contained in a 1-liter beaker at the rate of 500 ml/hr, by means of a sintered glass frit. The mixture was stirred at about 100 rpm with a magnetic stirrer. 0.1N NaOH was used to maintain a constant pH. In the 2nd method, no stirring was used; instead, ozone bubbles were spread by a 90 mm diameter sintered glass frit.

The ozonation of wastewater effluents was carried out in a reaction vessel of 6.5 cm diameter and 52 cm height, with a fritted glass filter at the bottom. A continuous flow of ozone was passed through the solution.

References: None cited.

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PH-29

Title: "Catalytic and Sonocatalytic Oxidations of Aqueous Phenol"

Authors: G.V. Smith, J.W. Chen & K. Seyffarth

Source: Proc. 5th Intl. Congress on Catalysis, Palm Beach, FL, Aug. 21-25, 1972, p. 893-903

Review: Addresses the oxidation of aqueous solutions of phenols (catechol, hydroquinone, resorcinol, quinone, and pyrogallol) via various combinations of high frequency ultrasound, Raney Ni and air with ozone.

Ozone Generation and Contacting: Ozone was generated from air using a Welsbach Ozonator T23 at a rate of 65 mg/hr. The contacting apparatus was a flat-bottomed tube, 2.25 in diameter x 16 in high, having a transducer mounted under the bottom. Ozone was bubbled through 200 ml (500 mg phenol/-liter) of aqueous phenol solutions over 3 hrs. Ultrasonics equipment was an 800 KHz Macrosonics Aerosol Generator Model 180-VF. Acoustic power output was 33 watts (average).

Discussion: No change in [phenol] is seen in the presence of activated Raney Ni and air without ultrasound. However, when about 65 mg of ozone/hr (1.15 mg/l) are bubbled through the phenol solution, a 28% decrease in [phenol] occurs. With insonation alone, an almost linear decrease of 63% in [phenol] occurs, and the combination of ultrasonic irradiation and ozone results in a decrease in [phenol] of 94%.

Combining Raney Ni and ultrasound (air atmosphere) causes approximately the same change as ultrasonic irradiation alone (60% decrease), but Raney Ni together with ozone decreases [phenol] 68%, compared with 28% for ozone alone. The lowest [phenol] after 3 hrs treatment (decrease of 95%) was reached by a combination of ultrasonic irradiation, ozone and activated Raney Ni. The combination of ozone and Raney Ni results in substantial loss of carbon, which suggests that this combination is effective in converting phenol to CO_2 while the other treatments (with the probable exception of ozone, Raney Ni and ultrasound for which there were no data) merely produce more highly oxidized species.

In the ozone experiments, the order of increasing reactivity is always O_3<Raney Ni/O_3<US/O_3<US/Raney Ni/O_3, but whereas US/O_3 is substantially more reactive than Raney Ni/ozone for phenol oxidation, the 2 treatments produce nearly identical rates of COD change.

Although [phenol] disappeared rapidly (40 mg/l, 200 mg, 0 mg of phenol after 2.5 hrs), COD values decreased rather slowly. The authors conclude that reaction of phenol to produce di- and trihydroxybenzenes as a 1st step is rapid; the 2nd step of aromatic ring rupture producing aliphatic acids is slower, and the 3rd step of production of CO_2 and water is slower still. Insonation of ozone produces species which homogeneously oxidize phenol to

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polyhydroxybenzenes but do not readily facilitate steps 2 and 3. Raney Ni must offer a lower energy surface pathway for step 3 and/or step 2 -- and it may also catalyze the decomposition of ozone.

References: 6.

PH-32

Title: "Alternative Methods of Phenol Wastewater Control"

Author: W.M. Throop

Source: J. Hazardous Materials 1:319-329 (1977)

Reviews methods for removing phenol (I) from large volume flow effluents by biological and chemical oxidation. Adsorption by activated carbon produces the lowest level of I in the final effluent, but is the most expensive treatment process. Oxidation by chlorine is effective, but needs careful control. ClO_2 may be a practical alternative. For very large effluent flows, ozonation is the least costly of the 3 oxidants which includes ozone, H_2O_2 and $KMnO_4$, but at small flows, all 3 are competitive in cost.

Biological treatment of I has a great number of operating problems (need for pH, N and P adjustment, temperature, sensitivity to shock loads, need to supply oxygen) and it is questionable whether concentrations <500 ppb can be produced consistently.

Activated carbon produces effluents with <1 ppb I, but the process requires 3,300 parts of carbon/part of phenol removed. Operational costs (1976 dollars) to treat 9 MM cu m/yr of wastewater to attain <1 ppb of I are estimated to be 15¢/cu m.

Chlorination requires a minimum dosage of 12 mg/l at pH 7.0 to 8.3 (Cl/I ratio 98/1) to produce an effluent containing non-detectable I. To treat a 25 cu m/day waste flow with chlorine would cost $50,000/hr, plus the capital cost for a chlorinator and chlorine contact chambers. Underchlorination produces chlorophenols.

[I] of 3 ppb have been attained from 500 mg/l concentrations using 4/1 H_2O_2/I at 49°, pH 5.5 and with 30 minutes retention time. But H_2O_2 must be treated with ferrous salt catalyst at pH 1.5, then raised to pH 11 to remove I.

At pH 8.5 to 9.5, $KMnO_4$ oxidizes I in 1 to 3 hrs (almost 90% oxidized in the first 10 minutes. An actual wastewater (25,000 cu m/day) having 123 ppb initial [I] was treated with 1, 5 and 10 mg/l doses of $KMnO_4$ over 20 minutes. A dosage of 10 mg/l (or a ratio of 80/1) $KMnO_4$/I was required to remove I. At 1976 prices, the cost to reach 1 ppb [I] in this wastewater is 0.8¢/cu m.

Ozonation experiments were conducted on a foundry waste (9MM cu m/yr) which had been presettled using an anionic polyelectrolyte and decanted (110 ppb [I]). With contact times of 5 minutes at 24°C, ozone dosages of 5.32 mg/l (O_3/I ratio 48/1), non-detectable levels of I were attained in the effluent. Only at an ozone dosage of 25.5 mg/l (O_3/I ratio of 200/1) was a trace amount of ozone residual detected, however. This indicates that compounds other than I are produced initially upon ozonation, which themselves are further oxidized during further ozonation.

Based on a power cost of 3¢/kwhr, the annual power cost to treat 9 MM cu m/yr from wastewater with ozone would be $6,000 to 13,500. Capital costs for ozone generation would be $125,000 (1976 prices).

Comparative costs to reduce I levels in foundry effluent (from 3 sources of 2.89, 1.3 and 2.4 mgd) to 1.5 ppb (1974 prices) are:

Chlorination: chlorination and contact tanks - $125,000
annual cost of chlorine - $40,000

$KMnO_4$: $65,000/yr.

H_2O_2: $75,000/yr.

Ozonation: $80,000-125,000 ozone generation and contacting
$4,000-9,000/yr power cost (at 2¢/kwhr)

C Adsorption: $9 MM initial capital cost
$1,100/yr operational cost

LITERATURE CITED (PHOTOPROCESSING) (PF)

PF-01 Anonymous, 1975, Kankocho Kogai Senmon Shiryo 10(4):63-74.

PF-02* Bober, T.W. & T.J. Dagon, 1974, "The Regeneration of Ferricyanide Bleach Using Ozone", Image Technology, Aug/Sept, p. 19-24.

PF-03* Bober, T.W. & T.J. Dagon, 1975, "Ozonation of Photographic Processing Wastes", J. Water Poll. Control Fed. 47(8):2114-2129.

PF-04* Dougherty, J.H., J.R. Ghia, W.D. Sitman & K.M. Peil, 1976, "Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Photographic Processing Subcategory of the Photographic Point Source Category", Rept. No. EPA 440/1-76/060 1, Group II, July. U.S. EPA, Effluent Guidelines Div., Washington, D.C. 20460.

PF-05* Garrison, R.L., C.E. Mauk & H.W. Prengle, Jr., 1974, "Cyanide Disposal by Ozone Oxidation", AFWL Report TR-73-212. Final Report for Period April 1972 - Nov. 1973. U.S. Air Force Weapons Laboratory, Kirtland Air Force Base, N. Mexico 87117.

PF-06 Garrison, R.L., C.E. Mauk & H.W. Prengle, Jr., 1975, "Advanced Ozone Oxidation System for Complexed Cyanides", in *Proc 1st Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 551-577.

PF-07* Gorbenko-Germanov, D.S., N.M. Vodop'yanova, N.M. Kharina, M.M. Gorodnov, V.A. Zaitsev, A.N. Koldashov & Yu. M. Murav'ev, 1975, "Ozonation of Silver-Containing Wastewaters From Enterprises Producing Photographic Chemicals", Khim. Prom. 2:21-23.

PF-08* Hendrickson, T.N., 1975, "Economical Application of Recovery & Pollution Control in the Photographic Film Processing Industry", in *Proc. First Intl. Symp. on Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, Editors. Intl. Ozone Assoc., Cleveland, Ohio, p. 578-586.

PF-09* Hendrickson, T.N. & L.G. Daignault, 1973a, "Treatment of Complex Cyanide Compounds for Reuse or Disposal." EPA Report No. EPA-R2-73-269, June. U.S. EPA, Washington, D.C. 20460.

PF-10* Hendrickson, T.N. & L.G. Daignault, 1973b, "Treatment of Photographic Ferrocyanide-type Bleach Solutions for Reuse and Disposal", J. Soc. Motion Picture & Television Engrs. 82(9):727-731.

PF-11 Lotz, R.E., 1972, "Chemical Wastes Generated by Air Force Photographic Operations", Air Force Weapons Lab Report No. AFWL-TR-72-125, September. U.S. Air Force Weapons Laboratory, Kirtland Air Force Base, N. Mexico.

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PF-12 Mauk, C.E. & H.W. Prengle, Jr., 1976, "Ozone with Ultraviolet Light Provides Improved Chemical Oxidation of Refractory Organics", Pollution Engrg., Jan. p. 42-43.

PF-02

Title: "The Regeneration of Ferricyanide Bleach Using Ozone"

Authors: T.W. Bober & T.J. Dagon

Source: Image Technology, 14(5):19-24 (1974)

Review: A method was developed using ozone gas to regenerate ferricyanide bleach overflow. The appreciable salt build-up commonly resulting from traditional persulfate treatment was eliminated, resulting in less waste.

If a processing lab operates 5.5 days/week, a total of 465 lbs of Na ferrocyanide would have to be regenerated/week, which would require 224 lbs of K persulfate or 39 lbs ozone/week, assuming 100% efficiency in both cases.

Capital costs for the ozone system are $18,700 (1970 prices) and operating costs are $650/year. Persulfate regenerating costs are $4,070/yr, at 20¢/lb for K persulfate. Ozone capital costs do not include plumbing, locating the system remote from photoprocessing machines, engineering, or special design features. The cash flow rate of return for using ozone instead of persulfate is estimated at 9%.

Ozone can be used economically to regenerate bleaches from Kodachrome film Process K-12 and Ektachrome Process CRI-1, but the potential benefits must be weighed against the high capital cost of ozonation equipment. Ozone regeneration of bleach is not economical for other processing baths. Malfunction of equipment is not a serious problem, in the experience of the authors.

Sparger contacting of ozone was used in these studies, and the authors recommend sintered glass tubular spargers or porous ceramic sparger plates. Teflon also would be satisfactory. Nylon, polyethylene and polypropylene failed after short periods of use. For tanks, polyester/glass was satisfactory. Polyethylene tanks tended to become brittle and rupture while full.

PF-03

Title: "Ozonation of Photographic Processing Wastes"

Authors: T.W. Bober & T.J. Dagon

Source: J. Water Poll. Control Fed. 47(8):2114-2129 (1975).

Review Various photographic processing solutions and chemicals were treated with ozone. Compared with biological treatment, ozone caused the breakdown

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of certain refractory developer components - such as color developing agents, Phenidone, EDTA, and hydroxylamine sulfate - producing more rapid and more complete breakdown. More complete degradation also was achieved with Kodak Elon developing agent, thiocyanate ion, and formate ion. Ozone had no significant effect on acetic acid, acetate ion or glycine, and ferricyanide ion degradation was slow and therefore impractical. Methanol was more rapidly broken down by biological treatment. Compounds degraded more or less equally by either process included hydroquinone, thiosulfate, sulfite, formalin, benzyl alcohol and ethylene glycol.

Contactor: Ozone (OREC generator, producing 70 g/hr) was bubbled through a cylindrical contact chamber (8 columns each 70 mm OD x 38 cm) via a sintered glass diffuser. Excess ozone was measured in a KI solution. Normally, 1 liter samples were ozonized. In most cases tests were conducted using 3-liter volumes. Additional experiments were run using a 62-inch high tank with a built-in gas dispersion apparatus and a 100-gal capacity, in which 80 gal batches of both activated sludge effluent and synthetic processing wastes were ozonated.

Results: Pure solutions of specific photographic chemicals were ozonized and the reduction in COD values determined. Pertinent data are given in Table 17. No attempt was made to optimize conditions for efficient ozone use with each solution. The purpose of these tests was to treat those chemicals not amenable to biological treatment with ozone.

Several synthetic photoprocessing effluents were prepared and ozonized. Pertinent results are listed in Table 18.

TABLE 17. OZONATION OF SYNTHETIC PHOTOPROCESSING EFFLUENTS (SAMPLE VOLUME = 3 LITERS)

Effluent	Initial COD, mg/l		Ozonation		gas flow rate	Reduction in COD value
	Calcd	Actual	dose g/hr	time (hrs)	(l/min)	
Eastman Color Print Film	2852	2750	0.47	5	1	50%
Ektaprint 3 chemicals	2600	2325	1.53	8	3	47%
(with bleach-fix regen.)			1.53	24	3	75%
Kodak ME-4 process	4832	4700	1.5	4	3	41%(a)

(a) no significant additional reduction resulted with longer treatment.

Ozone disinfection of effluent from an activated sludge plant treating only photographic processing waste also was studied. Complete disinfection was obtained with 30 minute contact time at ozone dosages of 1.5 mg/l/min fed to each of 8 consecutive columns. Residual [COD] was reduced from 50 to 30 mg/l, while 1 hr treatment reduced it to 17 mg/l.

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TABLE 18. OZONATION OF PHOTOPROCESSING CHEMICALS

Compound	Original Concn	Ozonation Time(hrs)	Ozonation Dose(g/hr)	Degree of [COD] Reduction
ethylene glycol (a)	1 ml/l	8	0.5	30-35%
hydroxylamine sulfate	1.0 g/l	12-16	1.88	77-78%
benzyl alcohol	1 g/l	24	1.6	85-90%
acetic acid	1.0 g/l	24	2.45	0%
N,N-diethyl-p-phenylenediamine mono-HCl (CD-1)	1.0 g/l	43	1.6	70%
2-amino-5-diethylaminotoluene mono-HCl(CD-2) (b)	1.0 g/l	16	0.7	60%
[4-amino-N-ethyl-N-(β-methane sulfonamidoethyl)-m-toluidine sesquisulfate monohydrate] (CD-3)	1.0 g/l	0.25	1.3	decolorized
	1.0 g/l	8(c)	1.3	51%
4-amino-3-methyl-N-ethyl-N-[β-hydroxyethyl] aniline sulfate (CD-4)	1.0 g/l	2	2.2	51%
	1.0 g/l	8	2.2	67%
Na thiosulfate	10 g/l	15	1.39	98%
Na thiosulfate	5 g/l	24	0.42	98%
glycine	1.0 g/l	24	1.0	0%
Na sulfite	6.2	2	1.9	97%(d)
hydroquinone	1.0	16	1.55	96%
"	1.0	4	1.55	54%
"	10.0	4	1.9	18%
p-Methylaminophenol sulfate (Elon)	2.0 g/l	16	1.4	70%
1-phenyl-3-pyrazolidinone	1.0 g/l	22	0.63	90%
disodium EDTA	1.0 g/l	24	1.23	70%
ammonium ferric EDTA	0.5 g/l	8	0.45	50%
Na formate	2.0	16	1.4	98%
formalin	5.0	24	2.28	53%
maleic acid	-	24	2.44	95%
"	-	4	2.44	58%
methanol	1.0	24	2.12	37%
K ferricyanide (e)	11.0	2	4.0	1%
"	11.0	100	4.0	30%
KCNS	1.0	2	1.55	86%
"	1.0	16	1.55	96%
"	5.0	8	1.45	94%

(a) No further analysis observed upon add 16 hrs trtmt with excess ozone. Utilization of ozone --30%.
(b) Degradation products resisted further breakdown.
(c) Ozone utilization --37%.
(d) The same result was obtained using air alone.
(e) Ozonation of K ferrocyanide regenerates K ferricyanide, which can be reused in the bleaching step.

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PF-04

Title: "Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Photographic Processing Subcategory of the Photographic Point Source Category"

Authors: J.H. Dougherty, J.R. Ghia, W.D. Sitman & K.M. Peil

Source: U.S. EPA Report No. EPA 440/1-76/060 1 (Group II) July, 1976, 187 pp. U.S. Environmental Protection Agency, Washington, D.C. 20460

Review: Effluent limitations and guidelines and standards of performance for photographic processing are set forth, along with supporting data and rationales for their development. Included are discussions of in-plant ferricanide bleach regeneration by ozonation and of end-of-pipe ozone treatment of various organic compounds.

Ferricyanide bleach regeneration by ozone proceeds by the following stoichiometric reaction:

$$2[Fe(CN)_6]^{-4} + H_2O + O_3 \rightarrow 2[Fe(CN)_6]^{-3} + 2(OH)^- + O_2$$

The pH of the system increases as the reaction proceeds. HBr can be added, furnishing both hydrogen ions and bromide, which is required in the bleaching process. Theoretically, 1 bromide ion is required/ferrocyanide ion that is oxidized to ferricyanide. Small amounts of sulfuric acid can be added if slight build-up of bromide ion occurs.

Waste destruction using ozone was successful for many compounds, including hydroxylamine sulfate, benzyl alcohol, color developer agent, thiosulfate, hydroquinone, Kodak Elon Developer Agent, Phenidone, EDTA, ferric EDTA, formate ion, formalin, maleic acid, Eastman Color Print effluent, Ektaprint 3 effluent, Flexicolor effluent and synthetic effluent from combined processes. Acetate and glycine do not respond to ozone treatment, and ethylene glycol, methanol, ferricyanide and ethylene diamine were only marginally treatable.

Ozone decomposition of ferrocyanide involves a number of competing reactions; free cyanide breaks down readily in the presence of ozone, to cyanate ion. This is apparently broken down by a combination of reactions, including both hydrolysis and oxidation.

Economics: A detailed analysis of total costs incurred in various wastewater treatments is included, but specific examples of costs of ozone treatment are not.

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PF-05

Title: "Cyanide Disposal by Ozone Oxidation"

Authors: R.L. Garrison, C.E. Mauk & H.W. Prengle, Jr.

Source: AFWL Report TR-73-212. Final Report for Period April 1972-Nov. 1973 (Feb. 1974). U.S. Air Force Weapons Laboratory, Kirtland Air Force Base, N. Mexico 87117

Review: A process was developed for complete destruction of total cyanide in influents as high as 100,000 mg/l, or below 1 mg/l, to produce effluents with total cyanide below the limits of detection. Influents were aqueous cyanide and complexed metal cyanide wastes from Air Force electroplating operations and color photographic film processing.

Laboratory studies showed that destruction of concentrated cyanide is limited by mass transfer of ozone, and destruction of dilute cyanide is limited by chemical reaction rate. Ozone at slightly elevated temperatures in the liquid (150°F) was more effective than ozone alone, but ozone with UV light was effective enough to permit design of a successful system. A 4 watt, 253.7 nm UV bulb, submerged in the liquid in the reactor, was the UV source.

A pilot scale prototype was designed, constructed and operated to destroy cyanide wastes to below the detectable limit. The conceptual design of a full scale system is included.

Wastewaters Studied: included Ni stripping, Cu plating, Cd plating, photographic bleach and photographic fixer, each treated by UV/ozone in low and high concentrations. In all cases, total [cyanide] in the effluents was below the detectable limit.

Experimental Details: Acrylic plastic was used for the reactor (it is transparent) and stainless steel and Al were used for portions of the system in contact with the dry gas phase. Synthetic wastes were studied first. Ozonation at pH 11.0 converted all CN^- to cyanate, after which acidification to pH 4 immediately hydrolyzed cyanate. Three lbs of ozone were found to react with 1 lb of free CN^-, except for Cu-containing solutions, in which the ratio was 2.5/1. Similar results were obtained using actual plating and photoprocessing wastes.

Prototype Reactor: 3 vertical countercurrent contact stages were used, each containing UV light sources and 420 RPM agitation. UV light was used only when the $[CN^-]$ was expected to be <50 mg/l or when Fe cyanide complexes were present. The prototype was designed to treat 0.5 gal/8 hrs of waste containing 40,000 mg/l of CN^-, or 15 gal/24 hrs of waste containing 4,000 mg/l of CN^-, or lower.

Each contacting stage was 12 inches in diameter and 16.5 inches tall. Six 15-watt tubular UV lamps (253.7 nm) were mounted vertically in each

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stage, 1 inch from the reactor sidewalls. A W.R. Grace LG-2-L2 ozone generator (oxygen feed) was used, producing 3.2% (by wt) ozone.

Prototype Results: With dilute cyanide wastes (photo bleach, photo fixer, Cu plating and Ni strip) containing 10 mg/l CN^-, at waste feed rates of 20 gal/day and UV lamps on in all 3 reactor stages, no CN^- was detectable in the second or third stages for any runs.

Four additional runs were made on concentrated wastes. For Cu plating waste, UV and heat (150°F) were used in the 3rd stage only (ozone only in the 1st and 2nd stages). The liquid feed contained 4,000 mg/l of CN^- (pH 11.5); the pH in stage 3 was controlled at 7 to 8 using sulfuric acid; the effluent contained <0.1 mg/l of CN^-. 2.4 wt % ozone was fed to the 3rd and 2nd stages (0.14 lb/day and 1.96 lbs/day, resp.) and off-gases from these stages were fed to the 1st stage (2.1 lbs ozone/day total). Approximately 1,600 mg/l of SS were formed. Over 99.5% of the CN^- was destroyed in the 1st stage, leaving only Fe-complexed cyanide.

Ni strip (4,000 mg/l of CN) was treated similarly with similar results. (0.16, 0.26 and 1.68 lbs/day of ozone were fed to the 3rd, 2nd and 1st stages, resp.). 97% to 99% of the CN^- was removed in the 1st stage. The treated effluent contained 130 mg/l of SS.

With photo fixer (700 mg/l of CN^-), 0.43, 0.43 and 1.23 lbs/day of ozone were fed to the 3rd, 2nd and 1st stages, resp. UV was used in stage 3 only, but 150°F was maintained in all 3 stages. The pH in stage 1 was controlled at 7 with NaOH. [CN^-] was reduced to 550 mg/l in stage 1, to 70 mg/l in stage 2 and to <0.2 mg/l in stage 3. Treated water contained 625 mg/l of SS.

Photo bleach (4,000 mg/l of cyanide complexed with Fe) was treated in 6 stages and 5.9% ozone was employed. 0.50, 0.38, 0.38, 0.50, 0.38 and 0.38 lbs/day of ozone were fed to the six 6 stages. UV was used in stages 5 and 6, and 150°F was maintained in all stages. [CN^-] leaving the 6 successive stages, resp., were 2,680, 1,630, 710, 105, 13 and <0.3 mg/l. About 1,900 mg/l of SS were produced.

In all 4 concentrated wastewater runs, 93% to 99% of the CNO^- also was destroyed.

Cost Estimates: A 3-staged system to treat 5 gpm of cyanide (50,000 mg/l total CN^-), allowing 10.7 hrs/contact stage and using UV and pH control in the 3rd stage only, and 7,560 lbs/day of ozone (from oxygen) is estimated to cost \$2.5 MM (plus liquid oxygen storage) and will use 1.35 megawatts of electricity. This unit would operate 24 hrs/day - 7 days/week.

For treating 1,000 gal/week in 5 24-hr days, ozone (210 lbs/day) would be generated from air and the installed cost is estimated at \$217,000. Operating costs would be 8 man hrs/week, 60 Kw of electrical power and \$5,000/yr in replacement UV lights.

PF-07

Title: "Ozonation of Silver Containing Wastewaters from Enterprises Producing Photographic Chemicals"

Authors: Gorbenko-Germanov, D.S., N.M. Vodop'yanova, N.M. Kharina, M.M. Gorodnov, V.A. Zaitsev, A.N. Koldashov, & Yu. M. Murav'ev

Source: Khim. Prom. 2:21-23 (1975)

The results of laboratory tests on the destruction of AgBr colloids and the complete oxidation of gelatin by ozone in dilute aqueous solutions are cited. Data are presented concerning the ozonation of model solutions of AgBr colloids and of solutions of photoemulsion produced by 2 Soviet chemical plants which simulate real wastewaters. On the basis of the data obtained, an economic estimate is made of a proposed method of ozonation of Ag-containing wastewaters in which >99% of the Ag is extracted with practically complete oxidation of the gelatin.

PF-08

Title: "Economic Application of Ozone for Chemical Recovery and Pollution Control in the Photographic Film Process Industry"

Author: T.N. Hendrickson

Source: *Proc. 1st Intl. Symp. on Ozone for Water and Wastewater Treatment*, R.G. Rice & M.E. Browning, Editors, Intl. Ozone Assoc., Cleveland, Ohio, 1975, p. 578-586.

Review: Ozone application in the treatment and the regeneration of ferricyanide bleach and bleach-fix is discussed, as well as ozone destruction of other photographic processing wastes that may violate effluent discharge limitations. Several case histories are described, including successful ozone treatment and regeneration of bleach by Photographic Corp of America (PCA), Berkey Photo, CBS Televison, and JOSR-TV (Nagano City, Japan).

Ozone Generator; The equipment (OzPAC) was designed by CPAC, Inc., Leicester, N.Y. The system has a capacity of 100 g/hr of ozone at 1.0 to 1.5% of ozone in air; this could be modified to supply up to 200 g/hr of ozone, with a concentration range from 0.75 to 1.5% in air.

Contact: Ceramic spargers with a pore size of approximately 100 μ located in the bottom of the waste treatment tanks. The same batch system was used for both waste treatment and ferricyanide bleach regeneration.

Results: Stoichiometrically, 20.2 lbs of sodium ferrocyanide decahydrate could be regenerated to 11.7 lbs of sodium ferricyanide by 1 lb of ozone. Bench top and pilot plant tests showed ozone oxidation efficiency to be nearly 100% for [ferrocyanide] >1.0 g/l. Destruction of complex cyanide compounds was not practical at room temperature. At Berkey Photo, about 220 consecutive 100-gal batch regnerations of the same ferricyanide bleaches have taken place, with the solution recycled.

When ozone was used in the laboratory rather than air to oxidize ferrous iron to ferric iron in bleach-fix (iron/EDTA) prior to reuse in the process bath, aeration time was reduced 50%. No degradation of the various miscellaneous organic additives in the "bleach-fix" soln was observed.

For chemical destruction, thiosulfate and sulfite were easily oxidized to sulfate by ozone. Sulfide compds produced in the process could precipitate traces of heavy metal ions, and toxicity was reduced by the oxidation of hydroquinone and Elon. Na, acetate, K acetate, and acetic acid were not effectively treated with ozone.

Case histories are given showing BOD and COD, removal of heavy metal ions, and decreased concentrations of metal chelating agents and of complex cyanides. [BOD-5] in JOSR-TV waste effluents were reduced from 1,500 mg/l to about 12 mg/l, and Fe, CN, Zn, Ag, and Cd levels lowered to within toxic level standards by ozone treatment.

Economics: Total investment at JOSR-TV was $34,000; at a savings of $6,000/yr, this will be repaid within 6 yrs by chemical savings. Berkey Photo bought 2 ozone generating units for about $41,000 (plus installation) with annual savings resulting from overall recovery of ferrocyanide, thiosulfate, sulfite, and silver amounting to about $25,000. CBS-TV showed a 2.5 to 3 yr payoff time.

For an average film processing laboratory, an OzPAC unit, sized for bleach regeneration only, could return the entire investment in about 24 months; for both chemical recovery and waste treatment, a 60-month payoff time would be expected.

References: None cited.

PF-09

Title: "Treatment of Complex Cyanide Compounds for Reuse or Disposal"

Authors: T.N. Hendrickson & L.G. Daignault

Source: U.S. EPA Report EPA-R2-73-269, June, 1973. U.S. EPA, Washington, D.C. 20460

Review: Ozone was evaluated versus other alternates for treating photofinishing solutions and wastes and was compared to electrolysis for ferrocyanide (bleach) regeneration, and precipitation and chlorination for treatment of effluents from color photoprocessing wastes.

Ozone Generator: Purification Sciences Incorporated, Geneva, N.Y., Model LOA-2; Flow: 0 to 20 SCFH; Output: 0 to 3 g/hr with pure oxygen.

Contacting Systems

1. For bench top regeneration the reactor was a hydrometer column; 18.5 inches high x 2.5 inches OD x 1/8 inch wall thickness and the sparger, Labpor gas dispersion tubes, polyethylene candles, medium porosity (Bal-Art Products, Pequannock, NJ).

2. For pilot plant regeneration the reactor was a clear Plexiglass column: 52 inches high x 3.5 inches ID x 0.25 inch wall thickness, together with a pump (March Manufacturing Co.; Model LC-2A, 115 volts, 60 cycle) and a flow meter (F.W. Dwyer Manufacturing Co.; Type VFA-34-BV, range 20 to 200 ml/min).

3. For bench top destruction the reactor was a Kimax 1 liter beaker and hot plate (Dylatherm Model 24202, 500 watts). Sparger was a Labpor gas dispersion tube, polyethylene candles, medium porosity. Reactor: Kimax Beaker, 1,000 ml, Hot Plate: Dylatherm Model 25202, 500 watts.

Results: Runs were made using simulated wastes (i.e., using laboratory grade reagents and photo bleaches from Ektachrome ME-4 & Kodachrome K-12 processors, with the results given in Table 19.

Cost: Cost of regeneration was estimated at $7,200 for equipment, labor and maintenance. Daily savings amounted to $22.90 or about 2.85¢/roll of film processed. Cost of destruction was estimated at $25,680 for equipment, labor and maintenance. Daily chemical costs were estimated at $7.65. An increase of 2¢/roll of film was anticipated.

Conclusions: Ozone treatment appears to be the best choice for control of complex cyanide pollution. Photographic bleaches containing ferro- and ferricyanide can be recovered and reused by either ozonation or electrolysis with similar process cost savings. The recovery is economically justified. Ferro- or ferricyanide can be removed effectively from wastewater by precipitation with a heavy metal (especially by Cd and Zn). Ferro- and ferricyanide destruction can be achieved either by ozone or chlorine oxidation in acid solution.

References: 81

PF-10

Title: "Treatment of Photographic Ferrocyanide-type Bleach Solutions for Reuse and Disposal"

Authors: T.N. Hendrickson & L.G. Daignault

Source: J. Soc. Motion Picture & Television Engrs. 82:727-731 (1973)

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TABLE 19. OZONATION OF SPENT PHOTOGRAPHIC FERROCYANIDE BLEACH SOLUTIONS

Operation	Ferrocyanide Concn. Initial	Ozone Feed	Reaction Conditions	Results
bench top regeneration	10 ± 0.01 g/l (1 liter)	2.36 g/hr 5 SCFH	pH adjusted w/HCl; run until ozone odor in off-gas	20.2 wt units ferrocyanide converted to 11.7 wt units ferricyanide (100% efficiency)
pilot plant regeneration	30 g/l (50 gal)	2% vol. 5 SCFH	50-150 m/min flow rate	for concn <1 g/l, rate of conversion is indirectly proportional to ozone flow (O_3 flow const.); no other data given
bench top destruction	0.01 M (500 ml)	5 SCFH	1) no pH or temp control 2) 5 g steel wool, 20 ml HCl 3) 20 ml HCl, 70°-90°C	little destruction some destruction at pH <3 temp <80°C - destruction to 0.003 in 30 min at >80°C - destruction to 0.001 in 18 min.

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Review: Methods to recover or destroy the complex cyanides found in photographic wastewater effluents were evaluated in laboratory studies by electrolysis, ozonation, chlorination, and heavy metal ion precipitation.

Recovery processes, directed toward producing a recovered bleach solution free from by-products that might affect bleaching, were carried out on the overflow of the concentrated working bleach tank. These resulted in 20.2 g of sodium ferrocyanide decahydrate being converted to 11.7 g of sodium ferricyanide with 1 g of ozone. There was a direct linear relationship between ozonation time and % conversion. Changes in pH did not affect the ozonation reaction rate. Ozone oxidation efficiency was near 100% for [ferrocyanide] >1.0 g/l.

The destruction of ferrocyanide was directed toward reducing the total [cyanide] to <2 mg/l, while producing only inert end-products. The diluted solution resulting from the carryover, on the emulsion, of bleach into the next process bath, as well as the tank overflow mentioned above, received this treatment. A combination of reactions was observed, with both oxidation and hydrolysis occurring. Cyanide molecules broke down into formate and ammonia, or CO_2 and nitrogen. The pentaferrate $[Fe(CN)_5]$ remaining from ferrocyanide hydrolysis was considered unstable, and should break down into ferric hydroxide. A nitroprusside intermediate was formed under slightly acidic conditions.

Ozone Generator: Ozone was generated at a rate of 10 g/hr for bleach regeneration processes, and 200 g/hr for cyanide destruction.

Contact: Ozonized air was sparged through the bleach from the bottom of the contact vessel (of which no further description was offered).

Procedure: Synthetic solutions were used to test the following 3 reaction procedures:

1) Ozone was bubbled into the sample with no pH adjustment or temperature control. Only slight changes in [ferricyanide] occurred.

2) The test solution was highly acidified (20 ml HCl); 5 g of steel wool catalyst was present. The complex cyanide underwent some decomposition, but the reaction was strongly pH-dependent. At pH 3.0, iron hydroxide and cyanate were produced, but very little decomposition occurred at pH 3.0.

3) The test solution was acidified with HCl (pH 1.5) and heated. Temperatures ranged from 70 to 90° C. Ozonation promoted a more complete destruction of the complex cyanide than did simple heating and aerating. Precipitation of the complex cyanides proceeded faster than their decomposition.

Economics: Costs were analyzed on the basis of a single hypothetical "combined average" processor*. Ozone generators, which produce 10 g/hr and 200 g/hr, cost $2,000 and $14,000, resp., in 1973.

An estimated savings of 2.8¢/roll of processed film could be realized by bleach regeneration with ozone, or 2.9¢/roll with electrolytic regeneration. Bleach destruction costs up to 7.5¢/roll (alkaline chlorination), with ozone destruction costing an estimated 2.2¢/roll.

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* Including the following processors: color negative film, color reversal film, color positive paper and color reversal paper. The replenishment rate was 200 ml/min for 800 rolls of "equivalent" color-negative film processing. [Sodium ferricyanide] in replenisher - 50 g/l. Bleach cost - $1.10/gal of fresh replenisher.

LITERATURE CITED --PLASTICS & RESINS (PL)

PL-01 Bauch, H. & H. Burchard, 1970, "Experiments to Improve Highly Odorous or Harmful Sewage With Ozone", Wasser Luft u. Betreib 14(4):134-137.

PL-02* Chen, K.Y. & R.W. Okey, 1977, "Ozone Effect on Synthetic Rubber Waste Treatment", Industrial Wastes, March/April, p. 46-48.

PL-03* Kwie, W.W., 1969, "Ozone Treats Wastestreams From Polymer Plant", Water & Sewage Works, Feb., p. 74-78.

PL-04* Linevich, S.N., I.M. Arutyunov, R.M. Siganashvin & V.A. Golosnitskaya, 1972, "Ozonization of Phenol- and Formaldehyde-Containing Wastewaters", Tr. Novocherkassk. Politekh. Inst. 249:12-20. Ref. Zh., Khim. (1972). Abstr. No. 20I346.

PL-02

Title: "Ozone Effect on Synthetic Rubber Waste Treatment"

Authors: K.Y. Chen & R.W. Okey

Source: Industrial Wastes, March/April 1977, 46-48

A 10 gpm pilot plant study using actual wastes is described. Wastewaters from emulsion polymerized GR-S rubber production (containing butadiene, styrene, K rosin soap, detergent, Na phosphate, NaOH, Cerelose, ferrous sulfate, $K_9P_2O_7$, cumene hydroperoxide, tertiary mercaptans, hydroquinone and N-phenyl-2-naphthylamine), primarily from the latex filtering step following coagulation with alum and settling, were studied (BOD 70 mg/l; COD 365 mg/l). The wastes were only slightly biodegradable (about 20%).

Ozone Generator: A laboratory model operating on air at a flow rate of 1.5 and 1.0 std cu ft/hr. [Ozone] was not specified.

Contactor: Bubbler type. Size unspecified.

Results: At 1.5 scfm, plant effluent [COD] was reduced from 365 mg/l to 160 in 40 minutes. With 350 mg/l added Na bicarbonate (effluent sample size not specified) [COD] was reduced to 85 mg/l in 40 minutes of ozonation. At 1.0 scfm of ozone, plant effluent [COD] was reduced 47%, but in buffered solution (with Na bicarbonate), reduction of [COD] was 70%.

Decomposition of ozone in water is very rapid above pH 8, and the efficiency of ozonation is reduced at low pH. Thus the optimum pH range for ozonation of these wastes is recommended at 6.0 to 8.5.

Ozone treated effluents had substantial influence on oxygen uptake, whereas untreated effluent had little. This indicates that ozonation of persistent organic compounds followed by conventional biological treatment would be the better way to treat many non-biodegradable organic compounds.

Upon ozonation, the distinct odor of butadiene-styrene was replaced by a milder scent of a "different kind". Turbid solutions became clear and suspended matter settled within 10 to 20 minutes of ozonation.

PL-03

Title: "Ozone Treats Waste Streams From Polymer Plant"

Author: W.W. Kwie

Source: Water & Sewage Works, Feb. 1969, p. 74-78

This is a laboratory study, with wastes from a synthetic polymer plant (plant products not identified) containing unsaturated organics and some Na 8-alkylnaphthalene sulfonate-2 (SANS), which is very resistant to biodegradation.

Ozone Generator: Welsbach Ozonator using oxygen

Contactor: 100 ml bubbler

Results: (1) COD of the monomer plant wastewater (3,340 to 910 mg/l) was reduced only when unsaturated wastes that react readily with ozone were used. Absorption of 5,400 mg/l ozone gave 90% COD removal in unspecified contact time.

(2) Additional reduction in COD values of ozonated samples was noted with time. A sample having 1,380 mg/l immediately after ozonation had 450 mg/l after 7 days of storage.

(3) Foaming ability, color and odor of these wastewaters were reduced after ozonation. Colloidal orange substances were transformed by ozone into an easily settling sludge.

(4) One aromatic ring of SANS was cleaved, however, the remaining aromatic ring was resistant to further ozonation. Ozonation did not increase the biodegradability of SANS.

References: 15

PL-04

Title: "Ozonization of Phenol- and Formaldehyde-Containing Wastewaters"

Author: Linevich, S.N., I.M. Arutyunov, R.M. Siganashvin & V.A. Golosnitskaya

Source: Tr. Novocherkassk. Politekh. Inst. 249:12-20 (1972). Ref. Zh., Khim (1972). Abstr. No. 20I346

Phenol and formaldehyde in wastewaters were ozonized. Humic acids were determined in the ozonized solns by UV and IR spectroscopy.

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LITERATURE CITED (PULP & PAPER) (PU)

PU-01* Abadie-Maumert, F.A., B. Fritzvold & N. Soteland, 1977, "The Norwegian Semi-Industrial Pilot Plant for Processing of Paper Pulp by Ozone". Presented at 3rd Intl. Symp. on Ozone Technol., Paris, France, May. Intl. Ozone Assoc., Cleveland, Ohio.

PU-02 Ancelle, B. & M. Plancon, 1966, "Bleaching Wood Pulp", French Patent 1,441,787, June 10. Chem. Abstr. 66:20152s.

PU-03* Anonymous, 1974, "Ozone Bleaching Pilot Plant Called Success", Paper Trade J., Feb. 4, p. 9.

PU-04* Bauman, H.D. & L.R. Lutz, 1974, "Ozonation of a Kraft Mill Effluent", TAPPI 57(5):116-119.

PU-05* Buley, V.F., 1973, "Potential Oxygen Application in the Pulp & Paper Industry", TAPPI 56(7):101-104.

PU-06 Clayton, D.W., N. Liebergott & T. Joachimides, 1971, "Evaluation of Ozone Treatment of Mechanical Pulp", Pulp & Paper Rsch. Inst. of Canada, Prog. Rept. 39, Oct. 1, p. 106-115.

PU-07* Furgason, R.R., H.L. Harding & M.A. Smith, 1973, "Ozone Treatment of Waste Effluent." Research Completion Report, OWRR Project No. A-037-IDA, Water Resources Inst., Univ. of Idaho, April. NTIS Report No. PB-220,008.

PU-08 Furgason, R.R., H.L. Harding, A.W. Langeland & M.A. Smith, 1974, "Use of Ozone in the Treatment of Kraft Pulp Mill Liquid Wastes. Part I. Color, Odor and COD Reduction". Am. Inst. Chem. Engrs. Symp. Series 70:139.

PU-09 Furgason, R.R., M.A. Smith & H.L. Harding, 1973, "Ozone Treatment of Pulp Mill Wastes", presented at Natl. Am. Inst. Chem. Engrs. Mtg., Vancouver, B.C., Sept.

PU-10* Hatakeyama, H., T. Tonooka, J. Nakano & N. Migita, 1967, "Ozonolysis of Lignin Model Compounds", Kogyo Kagaku Zasshi 70(12):148-152, 2348-2352.

PU-11* Hatakeyama, H., T. Tonooka, J. Nakano & N. Migita, 1968, "Degradation of Lignin with Ozone." Chem. Abstr. 70:12768 (1969). Kogyo Kagaku Zasshi 71(8):1214-1217.

PU-12* Hosokawa, J., T. Kobayashi & T. Kubo, 1975, "Bleaching of Pulp", Japan. Kokai 76,139,903, Dec. 2, 1976, Appl. 75/62,661, 26 May. Chem. Abstr. 86:57076 (1977).

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PU-13 Huriet, B. & P. Gelly, 1970, "Improvements to Processes for the Decoloring of Effluents From Kraft Pulping", French Patent 1,599,588 (July 15.); Abstr. Bull. Inst. Paper Chem. 42:4413 (1971).

PU-14* Jackowski, J., 1970, "Ozone Treatment of Pulp and Paper Mill Effluents", Private Communication, Nov. 1970 to I. Gellman. Noted in Nat'l. Council of the Pulp and Paper Industry for Air and Stream Improvement, Tech. Bull. #269, Jan. 1974, by R.C. Whittemore (p. 2).

PU-15 Josephson, J., 1974, "Cleaning Up: Paper Industry's Mess", Env. Sci. & Technol. 8(1):22-24.

PU-16 Jurgensen, M.F. & J.T. Patton, 1977, "Energy and Protein Production From Pulp Mill Wastes", Annual Rept., 6/15/76-6/15/77 under U.S. ERDA Contract E(11-1)-2983. See also Progress Reports for the periods 6/15/77-9/15/77 and 9/15/77-12/15/77 under same contract.

PU-17 Jurgensen, M.F. & J.T. Patton, 1977a, "Energy and Protein Production From Pulp Mill Wastes", Prog. Rept. (Dec. 15, 1976-Mar. 15, 1977) under Contract EY-76-S-02-2983, U.S. Dept. of Energy, Washington, D.C.

PU-18 Jurgensen, M.F. & J.T. Patton, 1977b "Energy and Protein Production From Pulp Mill Wastes", Annual Rept. (June 15, 1976-June 15, 1977) under Contract EY-76-S-02-2983, U.S. Dept. of Energy, Washington, D.C.

PU-19 Jurgensen, M.F. & J.T. Patton, 1977c, "Energy and Protein Production From Pulp Mill Wastes", Prog. Rept. (June 15, 1977-Sept. 15, 1977) under Contract EY-76-S-02-2983, U.S. Dept. of Energy, Washington, D.C.

PU-20 Jurgensen, M.F. & J.T. Patton, 1977d, "Energy and Protein Production From Pulp Mill Wastes", Prog. Rept. (Sept. 15, 1977-Dec. 15, 1977) under Contract EY-76-S-02-2983, U.S. Dept. of Energy, Washington, D.C.

PU-21* Kamishima, H. & I. Akamatsu, 1973, "Attempts to Modify the Activated Sludge Process for Sulfite Pulp Wastewater", Japanese TAPPI 27(9):449. Abstr. Bull. Inst. Paper Chem. 44(10): 10878 (1974); 44(8):368 (1974).

PU-22* Kamishima, H. & I. Akamatsu, 1974a, "Ozone-Activated Sludge Treatment of Sulfite Pulp Wastewater. Mechanism of BOD Removal, Treatment conditions and Sequential Treatment". Japanese TAPPI, 28(8):35-44.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

PU-23 Kamishima, H. & I. Akamatsu, 1974b, "Ozone-Activated Sludge Treatment of Sulfite Pulp Wastewater". Japanese TAPPI 28(8):368. Abstr. Bull. Inst. Paper Chem. 45(5):4865 (1974).

PU-24 Katai, A.A. & C. Schuerch, 1966, "Mechanism of Ozone Attack on a Methyl Glucoside and Cellulosic Materials." J. Poly. Sci., Part A-1, 4:2683-2703.

PU-25* Katuscak, S., A. Hrivik & M. Mahdalik, 1971a, "Ozonization of Lignin, Pt. I. Activation of Lignin with Ozone", Papper och Trä 9:519-523.

PU-26* Katuscak, S., I. Rybarik, E. Paulinyova & M. Mahdalik, 1971b, "Ozonation of Lignin, Pt. II. Investigation of Changes in the Structure of Methanol Lignin During Ozonation." Papper och Trä 11:665-670.

PU-27* Kiryushina, M.F. & D.V. Tishchenko, 1968, "Soda Lignin III. Lignin-Carbohydrate Bond in Soda Lignin From Hardwoods", Zhur. Priklad. Khim. (Leningrad) 41(8):1848-1853. Chem. Abstr. 70:12767p (1969).

PU-28* Kobayashi, T., J. Hosokawa & T. Kubo, 1976, "Bleaching of Pulp With Ozone", Japan. Kokai 76,139,902, Dec. 2, Appl. 75/62,660, May 26, 1975.

PU-29 Lantican, D.M., W.A. Cote, Jr. & C. Skaar, 1965, "Effect of Ozone Treatment on the Hygroscopicity, Permeability and Ultrastructure of the Heartwood of Western Red Cedar", Indl. Engrg. Chem., Prod R&D 4(2):66-70.

PU-30 Liebergott, N., ca. 1969, "Paprizone Treatment. A New Technique for Brightening and Strengthening Mechanical Pulps." Publication Not Identified.

PU-31 Liebergott, N., 1975, "Use of Ozone in the Pulp & Paper Industry for Pulp Bleaching." in *Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 614-624.

PU-32 Melnyk, P.B. & A. Netzer, 1976, "Reactions of Ozone With Chromogenic Lignins in Pulp and Paper Mill Wastewater", in *Proc. Sec. Intl. Symp. on Ozone Technol.*, R.G. Rice, P. Pichet & M.-A. Vincent, Eds. Intl. Ozone Assoc., Cleveland, Ohio, p. 321-335.

PU-33 Moergeli, B., 1973, "Possible Uses of Filtration in the Clarification of Residual Wastewater." Wochenbl. Papierfabr. 101(22):875. Chem. Abstr. 80(12):63609c (1974).

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PU-34* Moore, W.E., M. Effland, B. Sinha, M.P. Burdick & C. Schuerch, 1966, "The Resistance of Hemicelluloses in Wood Fiber to Degradation by Ozone", TAPPI 49(5):206-209.

PU-35 Mueller, J.C. & C.C. Walden, 1970, "Microbiological Utilization of Sulfite Liquor", British Columbia Research Report 323.

PU-36 Nakano, J. & N. Migita, 1968, "Degradation of Lignin With Ozone", Kogyo Kagaku Zasshi 71(8):1214-1217. Chem. Abstr. 70:12761n (1969).

PU-37 Nebel, C. *et al.*, 1974a, "Ozone Decolorization of Effluents From Secondary Effluents", Paper Trade J. 158(4):24.

PU-38* Nebel, C., R. Gottschling & H.J. O'Neill, 1974b, "Ozone: A New Method to Remove Color in Secondary Effluents". Pulp & Paper 48(10):142-145.

PU-39* Nebel, C., R.D. Gottschling & H.J. O'Neill, 1974c, "Ozone Decolorization of Pulp and Paper Mill Secondary Effluents", in *Proc. 7th Mid-Atlantic Indl. Wastes Conf.*, Drexel Univ., Philadelphia, Pa. p. 161-187.

PU-40 Nebel, C., R.D. Gottschling & H.J. O'Neill, 1975, "Ozone Decolorization of Secondary Pulp & Paper Mill Effluents." in *Ozone for Water & Wastewater Treatment*, R.G. Rice & M.E. Browning, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 625-651.

PU-41* Neimo, L., H. Sihtola, O. Harva & A. Sivola, 1967, "Graft Copolymers of Cellulose. Polymerization Initiated by Decomposition of Cellulose Peroxides." Papper och Trä 8:509-516.

PU-42 Ng, K.S., J.C. Mueller & C.C. Walden, 1978, "Ozone Treatment of Kraft Mill Wastes", J. Water Poll. Control Fed. 50(7):1742-1749.

PU-43 Osawa, Z. & C. Schuerch, 1963a, "The Action of Gaseous Reagents on Cellulosic Materials. I. Ozonization and Reduction of Unbleached Kraft Pulp", TAPPI 46(2):79-84.

PU-44* Osawa, Z., W.A. Erby, K.V. Sarkanen, E. Carpenter & C. Schuerch, 1963b, "The Action of Gaseous Reagents on Cellulosic Material. II. Pulping of Wood with Ozone". TAPPI 46(2):84-88.

PU-45* Ottman, R., 1972, "Ozonation of Kraft Pulp & Paper Effluents", Private Communication.

PU-46* Pristupa, A.M., 1974, "Treatment of Industrial Effluents and Gaseous Discharges in U.S. Industries", Bumazhn. Promy. (Moscow) 12:23-26.

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PU-47 Samuelson, O., G. Grangård, K. Jonsson & K. Schramm, 1953. Svensk. Papperstidn. 56:779-784.

PU-48 Secrist, R.B. & R.P. Singh, 1971, TAPPI 54(4):581.

PU-49 Smith, M.A. & R.R. Furgason, 1976, "Use of Ozone in the Treatment of Kraft Pulp Mill Liquid Wastes. Part II. Biodegradation", in Proc. Sec. Intl. Symp. on Ozone Technol., R.G. Rice, P. Pichet & M.-A. Vincent, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 309-320.

PU-50 Soteland, N. & K. Kringstad, 1968, "The Effect of Ozone on Some Properties of High Yield Pulps". Norsk Skogindustri 22(2):46-52.

PU-51 Soteland, N., 1971, "The Effect of Ozone on Some Properties of Groundwoods of Four Species. Part 1." Norsk Skogindustri 25(3):61-66.

PU-52 Soteland, N., 1974, "Bleaching of Chemical Pulps with Oxygen and Ozone", Pulp & Paper Mag. of Canada 76(4):91-96.

PU-53 Soteland, N. & V. Loras, 1974, "The Effect of Ozone on Mechanical Pulps", Norsk Skogindustri 28(6):165-169.

PU-54 Stern, A.M. & L.L. Gasner, 1974, "Degradation of Lignin by Combined Chemical and Biological Treatment", Biotech. Bioengrg. 16:789-805.

PU-55 Tuggle, M.L., 1972, "Reactions of Ozone With Reduced Sulfur Compounds Present in Kraft Mill Gaseous Emissions", Natl. Council of the Paper Industry for Air & Stream Improvement, Tech. Bull. No. 58, Feb.

PU-56 Tyuftina, V.I., 1971, "Reduction of Effluent Color Intensity by Ozonization", Sb. Tr. VNII Gidroliza Rast. Mater. (USSR) 19:209. Abstr. Bull. Inst. Paper Chem. 42:11444 (1972).

PU-57* Watkins, S.H., 1973, "Coliform Bacteria Growth and Control in Aerated Stabilization Basins". EPA Report No. EPA/660/2-73-029, Dec., p. 220-221.

PU-58* Whittemore, R.C. & J.J. McKeown, 1974, "Preliminary Laboratory Studies of the Decolorization and Bactericidal Properties of Ozone in Pulp and Paper Mill Effluents." Nat'l Council of the Paper Industry for Air & Stream Improvement, Inc., Technical Bulletin #269, January (40 pages).

PU-59 Wigren, G.A., 1965, "Bleaching of Pulp in a Chlorine-containing Bath Treated with Ozone", German Patent #1,293,875, January.

PU-01

Title: "The Norwegian Semi-Industrial Pilot Plant for Processing of Paper Pulp by Ozone".

Authors: F.A. Abadie-Maumert, B. Fritzvold & N. Soteland

Source: Presented at 3rd Intl. Symp. on Ozone Technol., Paris, France, May 1977. Intl. Ozone Assoc., Cleveland, Ohio.

Although the 1st research on the use of ozone for processing paper pulp dates from 1912, it is only since 1967 and the publication of the first work of the Norwegian Institute of Paper Research that laboratories in the major industrial countries have started to take an active interest in the possibilities of using ozone in the paper industry.

In 2 fields - the improvement of mechanical properties of mechanical pulps and the bleaching of chemical pulps - excellent laboratory results have been obtained, which open wide perspectives from the points of view of technology and the environment, for methods using ozone are considerably less polluting than traditional methods.

The results of laboratory research have been so promising that the Norwegian Institute for Paper Research, 5 of the biggest Norwegian paper companies, and the mechanical engineering company Myrens Verksted have collaborated in the construction of a semi-industrial plant for the processing of paper pulp by ozone.

The plant processes a maximum of 200 kg of mechanical or chemical pulp/hr with 6 kg of ozone. It is integrated into an existing paper pulp factory, which enables the processed pulp to be treated under industrial conditions. Oxygen is used for the production of ozone. The processing of the pulp takes place in a reactor, which operates continuously at ambient temperatures, and without overpressure, a prototype of a future industrial plant.

As this is a case of application of an entirely new technique to a traditional industry, particular attention has been paid to safety and control. The method adopted for destruction of the last residues of ozone has proved to be satisfactory.

The plant has been in operation since May 1976, and is at present undergoing its 2nd test campaign. It has provided a means of verifying the promising results obtained in the laboratory on a semi-industrial scale. In some cases results even better than those obtained in the laboratory were achieved.

The use of ozone-treated mechanical pulp has provided, among other things, for production of newspaper without chemical pulp and its printing on rapid rotary presses.

Since it was started up, the plant has been in regular service for tests, not only for its promoters but also for foreign paper companies. It opens up interesting prospects for the production of bleached bisulfite pulps and semi-bleached sulfate pulps without the use of chlorine, as well as for the development of use of different types of mechanical pulps for the production of printing paper, absorbent paper and cardboard.

The paper pulp industry represents a considerable potential market for ozone. The future of its use in the paper industry depends on the construction of ozone production plants of sufficient capacity, and above all on the possibilities of producing ozone at a cost such that it becomes competitive with other techniques used at present.

PU-03

Title: "Ozone Bleaching Pilot Plant Called Success"

Author: Anonymous

Source: Paper Trade J., Feb. 4, 1974, p. 9.

Ozone bleaching of wood pulp is said to be a step closer to commercialization now that successful pilot plant work has been completed in a joint effort by Scott Paper, W.R. Grace & Co., and Improved Machinery.

A single-stage 15 ton/day continuous reactor was operated using mixed hardwood kraft pulp at Scott's pulp mill at Muskegon, Mich. Ozone in oxygen carrier gas was passed through a fluffed moving bed of pulp where the ozone was stripped out and the carrier gas then recycled to the ozone generator.

The kinetics of the reaction of ozone with pulp lignin were established as well as purification requirements of the carrier gas for re-entry to the ozone generator.

The economics as well as the pollution abatement potential of ozone bleaching appear to make the process an attractive alternate for conventional hardwood bleaching.

PU-04

Title: "Ozonation of a Kraft Mill Effluent."

Authors: H.D. Bauman & L.R. Lutz

Source: TAPPI 57(5):116-119 (1974)

The P.H. Glatfelter Co. plant at Spring Grove PA produces about 500 tons/day of fully bleached kraft pulp from both hard and soft woods and about 600 tons/day of fine papers. Wastewaters from the pulp mill, bleach plant and paper plant are combined and given primary treatment and contact stabilization, activated sludge secondary treatment. Ozonation studies were conducted only on the secondary effluent because the high BOD before secondary treatment greatly increased ozone demand.

The secondary effluent (15 mgd) is consistently low in BOD (10 to 2 mg/l, average 5) and SS (50 to 12 mg/l, 25 average), but high in COD (typically 225 mg/l).

Ozone Generator: A Cochrane Div. of Crane Co., vertical tube unit produced 80 g/hr of ozone from oxygen and 40 g/hr from air. Using oxygen feed, power costs to produce ozone were 3.5 kwhr/lb of ozone, consistently.

Contact Towers: 4 13-ft high towers fabricated from 8-inch schedule 40 steel pipe. Ozone was introduced through 2-inch stainless steel spargers, one/tower, about 1 ft above the bottom of each tower. The liquid columns were 11 ft deep, and foam overflow outlets were provided. However, foaming was never a problem and no excess ozone was wasted from the vents. Most of the study was done at 4 gpm flow rates, which resulted in 30 minute total retention time, or about 7 min/tower. Gas flow was divided and regulated so that 40% of the ozone was applied in Tower 1, 30% in Tower 2, 20% in Tower 3 and 10% in Tower 4.

In preliminary studies which were up to 1 day of continuous ozonation, allowing up to 2 hrs continuous running at each level of ozone applied, it was found that nothing was gained by exceeding a total ozone dosage of 40 mg/l, and very little by exceeding 30 mg/l. SS were removed by flotation and foam removal. Almost no bacteria were killed at ozone doses up to 20 mg/l. However when bactericidal action began, coliform organisms appeared to be selectively destroyed. At 30 mg/l ozone, 60% to 80% reduction in coliform organisms was achieved, and essentially 100% at 40 mg/l; however, the total bacterial count remained surprisingly high (numbers not presented).

During preliminary studies with 5-μ mean pore size spargers and air feed, the spargers became plugged with $CaCO_3$ after a few hrs of running time. They could be cleaned with dilute HCl, but this would have prevented extended runs. Spargers with 20-μ mean pore sizes were substituted, which extended the running time to at least 72 hrs before plugging occurred. Using oxygen feed to the generator, even the 20-μ spargers plugged with $CaCO_3$ in about 24 hrs. The only solution to this problem was daily acid cleaning.

Eight replicate ozonation runs using 20-μ spargers produced 60% to 65% color reduction at 30 to 40 mg/l ozone dosages. Dosages of 20 to 30 mg/l caused 100% increases in BOD. When oxygen was used as feed gas, the effluent contained nearly 40 mg/l of dissolved oxygen, which was usually double the BOD of the ozonized effluent. Air feed increased the effluent BOD, but not the DO.

In other experiments, the [ozone] in the gas streams introduced to the contacting towers was varied (0.45% at 10 mg/l of applied ozone, 0.90% at 18 mg/l, 1.35% at 30 mg/l and 1.8% at 38 mg/l). Color reduction depended on the amount of ozone applied and was nearly independent of dose gas concentration.

Multiple regression analyses indicated that the only significant variables affecting color removal are: [applied ozone], initial color, COD, SS and units of color lost.

In an extended ozonation run, 80% color reduction was attained after 80 mg/l of ozone dosage, but about 30 mg/l of color remained even after 300 mg/l of ozone dosage. The BOD rose from 10 to 24 mg/l at 40 mg/l of ozone, remained at 20 to 25 mg/l up to 200 mg/l of ozone dosage, and decreased to 10 mg/l at 280 mg/l ozone dosage. About 99% of the coliform bacteria were killed by 40 mg/l of ozone and 99% of the total bacteria were killed by 100 mg/l of ozone.

Capital costs to treat 15 mgd with up to 40 mg/l of ozone (from oxygen) are estimated at $1 to 1.5 million. The ozonation plant would require about 5 kwhr/lb of ozone and would produce ozone at $0.25/lb.

With 15 mgd of an effluent whose color is <1,000 mg/l, COD 200 mg/l, SS <50 mg/l from 500 tons/day pulp plant and assuming electrical power at $0.015/kwhr, the operating costs at various ozone dosages are as follows:

mg/l Ozone	Color of Ozonated Effluent	Operating Cost	
		Yearly	Per Ton of Pulp
10	300-450	$121,500	$0.675
20	250-350	$243,000	$1.35
30	150-200	$364,500	$2.03
40	125-175	$486,000	$2.70

PU-05

Title: "Potential Oxygen Application in the Pulp and Paper Industry"

Author: V.F. Buley

Source: TAPPI 56(7):101-104 (1973).

High purity oxygen is on the fringes of numerous process applications in the pulp and paper industry. Interest in oxygen continues to be strong as new and old processes in the mills come under renewed investigation. This paper describes several developments in oxygen processes suitable for pulp mill applications. Specifically, weak black liquor oxidation, ozonation of pulp mill wastes, and pipeline reactors for the treatment of pulp mill liquor wastes are discussed.

PU-07

Title: "Ozone Treatment of Waste Effluent"

Authors: R.R. Furgason, H.L. Harding & M.A. Smith

Source: Research Technical Completion Report, OWRR Project No. A-037-IDA, Water Resources Research Inst., University of Idaho, April 1973. NTIS Rept. No. PB-220,008.

Review: The report describes a portable ozone test unit and several field tests made with the unit. Details of the portable test unit are as follows:

Reactor Volume	2 gal
Reactor Residence time	1-20 min
Feed Rate	0-1.5 gpm
Ozone Production	12 g/hr
Contactor	Venturi type

Experimental: The unit was light and easily moved in a van or pickup truck and required only 110 v of electricity, cooling water and the material to be treated for its operation.

Effluents from the Potlatch Forests Inc. kraft pulp mill at Lewiston, Idaho were treated. Waste streams from the bleach plant, total plant, primary clarifier and the extended aeration secondary system were tested. Since few differences were noted in color and reductions in [COD] or odor removals, the bulk of the data was taken on the primary clarifier output.

Color of the sulfite liquor changed dramatically from dark chocolate brown to light straw yellow in 5 min. At the same time the strong S-laden odor disappeared entirely. Reduction in [COD], however, was far less spectacular, being 10% to 15% in 5 min (sometimes up to 30%). The ozonized organic material was more biodegradable. Thus ozonation should precede secondary biological treatment and should not be used as a post- or tertiary treatment (alone).

Conclusions: The portable ozone unit has demonstrated its ability to obtain information, but a larger ozonator should be incorporated into the unit; other methods of contacting, however, should also be considered.

Economics: Preliminary estimates indicated costs to be 30¢/1,000 gal for decolorization and deodorization with a full sized plant (size not specified) but the authors recommend further tests on larger scale to refine these estimates.

PU-10

Title: "Ozonolysis of Lignin Model Compounds."

Authors: H. Hatakeyama, T. Tonooka, J. Nakano, & N. Migita

Source: Kogyo Kagaku Zasshi, 70(12):148-152, 2348-2352 (1967)

Review: The mechanism of degradation of the guaiacyl nucleus of lignin is discussed on the basis of the ozonolysis reaction products obtained from model experiments, using vanillyl alcohol and veratryl alcohol. These corresponded to the terminal and internal guaiacyl groups of the lignin structure. Paper chromatography and thin layer chromatography were used to separate the reaction products.

When free phenolic hydroxyl groups were present, the main ozonolysis reaction involved opening of the aromatic ring to give a muconic acid derivative; this was further degraded to maleic acid or oxalic acid. Where the phenolic OH groups in non-terminal positions were blocked, the ether group in the position para to the side chain was thought to be broken before the aromatic ring was opened.

Ozone Generator: Ozone was generated by introducing about 300 ml of oxygen/min into an ozone generator at an applied voltage of 15,000 v. The ozone was produced at a concentration of about 3 vol %.

Contact: The reactions were performed under both acidic and alkaline conditions. Vanillyl or veratryl alcohol was dissolved in a 3-necked flask, and ozone passed into the flask with cooling in ice and stirring. Reaction time was 5 hrs under acidic conditions, 2 hrs under alkaline conditions.

References: 6

PU-11

Title: "Degradation of Lignin with Ozone"

Authors: H. Hatakeyama, T. Tonooka, J. Nakano & N. Migita

Source: Kogyo Kagaku Zasshi 71(8):1214-1217 (1968). Chem. Abstr. 70:12766n (1969)

Four g of Ca lignosulfonate (I) in 50 ml H_2O was oxidized at 0° with 3 vol % of oxygen. Amounts of carbonyl, CO_2H, phenol and methoxyl ($^-$OMe) were determined on oxidized I. With oxidation, CO and CO_2H increased and PhOH and $^-$OMe decreased. The decrease in PhOH and $^-$OMe was accounted for by the postulate that the catechols resulting from demethylation of guaiacyls are immediately oxidized to muconic acid-type structures. Decomposition rates of the aromatic nucleus of I at each oxidation time under the above conditions were as follows: 18.5 (0.25), 34.5 (0.5), 38.7 (1.0), 41.6 (2.0), 46.3 (3.0), 48.9 (4.0) and 53.0% (5.0 hrs). About 90% of the CO_2H present in I oxidized at 0° for 5 hrs was that derived from the aromatic-nucleus scission of I.

PU-12

Title: "Bleaching of Pulp"

Authors: J. Hosokawa, T. Kobayashi & T. Kubo

Source: Japanese Kokai 76,139,903, Dec. 2, 1976, Appl. 75/62,661, 26 May 1975. Chem. Abstr. 86:57076 (1977)

Water containing pulp was bleached rapidly with ozone in CCl_4. Thus, 30 g kraft pulp sheet was sprayed with 45% water, suspended in 450 ml of CCl_4, and treated with oxygen containing 1% (vol) of ozone at 30° and 200 ml/min to prepare 94% pulp having a whiteness degree of 80%.

PU-14

Title: "Ozone Treatment of Pulp and Paper Mill Effluents"

Author: J. Jackowski

Source: Private Communication, Nov. 1970, to I. Gellman. Noted in Natl. Council of the Pulp and Paper Industry for Air & Stream Improvement, Tech. Bull. #269, Jan. 1974, by R.C. Whittemore (p. 2)

"500 mg/l of ozone added to a waste resulted in very little reduction in [BOD], but greater than 50% reduction in color from both a paper mill and a pulp mill effluent."

PU-21

Title: "Attempts to Modify the Activated Sludge Process for Sulfite Pulp Wastewater"

Authors: H. Kamishima & I. Akamatsu

Source: Jap. J. Technical Assoc. Pulp & Paper Indus., 27(9):449 (1973).

Review: Removals of TOC, COD, lignin and color of activated sludge (AS) treated alkaline extraction effluents from the bleaching of kraft pulp were improved by ozonation of the effluent. Subsequent AS treatment resulted in adequate BOD removal. Very little lignin was adsorbed from the ozonated effluent by activated carbon.

PU-22

Title: "Ozone Activated Sludge Treatment of Sulfite Pulp Wastewater. Mechanism of BOD Removal, Treatment Conditions and Sequential Treatment"

Authors: H. Kamishima & I. Akamatsu

Source: Japanese TAPPI, 28(8):35-44 (1974).

Review: Deals with BOD removal and treatment conditions in activated sludge treatment of the ozonized liquor of diluted black liquor. Results obtained were as follows:

(a) BOD removal rate was illustrated by the 2-phase theory of the equation. When initial BOD was around 600 mg/l, the reaction rate of BOD was first order, and when initial BOD was from 100 to 200 mg/l, it followed second order kinetics.

(b) BOD removal efficiency of more than 90% was achieved at less than 0.5 kg of BOD/kg of MLVSS/day, as well as that of the other pulping wastes.

(c) Sludge yield was more or less the same as that of other pulping wastes.

(d) In ozonized liquor containing 4.0 to 15 mg of ozone, BOD removal efficiency did not decrease at loadings of <0.4 kg of BOD/kg of MLVSS/day, but largely decreased at the higher BOD loading.

Sequential ozone-activated sludge treatment of diluted black liquor was studied and it was found that total removal efficiencies of COD (Mn) and BOD depended upon removal efficiencies of ozone treatment and activated sludge treatment.

When the remaining ozone in the effluent of stirring treatment and gas supplied to the aeration tank were 0.4 mg/l and 0.08 mg/l, resp, total removal efficiencies of COD (Mn) and BOD were 66.6% and 87.5%, with nearly satisfactory results.

Removal of lignin and color depended on ozone treatment and their total removal efficiencies were 66.6% and 81.5%, resp.

Economics: None mentioned.

References: 13

PU-25

Title: "Ozonization of Lignin, Part 1. Activation of Lignin with Ozone"

Authors: S. Katuscak, A. Hrivak, & M. Mahdalik

Source: Papper och Trä 9:519-523 (1971a).

Review: Polymerization reactions are initiated by hydroperoxide groups formed during the ozonation of various lignins. The kinetics and chemical natures of the functional groups formed by ozonation of lignins (in both solid state and dissolved in organic solvents) were studied. The lignins used included methanol-lignin (I), HCl-lignin (II), and CH_2N_2-methylated-HCl-lignin.

The ozonation of I was more rapid than that of II, with the rate of formation of active functional groups in I being 14 times greater than that of II. The solvent used for ozonation influenced the content of active functional groups, with low values being obtained in water, and higher values in acetic acid and methanol. The increased active functional group content was due solely to ozone. Active functional groups (not identified) were less stable at elevated temperatures. The decomposition half-life in the temperature range of 60° to 80°C varied from 2.5 to 20 minutes.

Ozone Generator: The source of ozone used was not described.

Contact: The lignins were ozonized either as dry solids or in suspension with protogenic solvents, at an oxygen flow rate of 600 ml/min and [ozone] of 39 mg/l. In the dry state the ozonation reaction occurred on a sintered glass filter with a diameter of 7 cm, at 20°C.

References: 37

PU-26

Title: "Ozonation of Lignin, Part II. Investigation of Changes in the Structure of Methanol Lignin During Ozonization."

Authors: S. Katuscak, I. Rybarik, E. Paulinyova, & M. Mahdalik

Source: Papper och Trä 11:665-670 (1971b)

Review: Changes in structure of lignin macromols were investigated by studying low molecular weight methanol-lignin during its reaction with ozone in the dry state. Spectral methods and vapor pressure osmometry detected changes in UV, IR and NMR spectra, and in average molecular weight of the lignin.

Low molecular weight methanol-lignin was very reactive when treated with ozone. The aromatic rings were the first to be attacked, producing oxidation reaction products and causing a gradual decrease in the average molecular weight. At least part of the active oxygen in the ozonized lignins is bound as hydroperoxide groups because neither quinonoids nor ozonides can initiate polymerization reactions.

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Rapid decrease in molecular weight occurs within the first 5 minutes of ozonization (210 molecular weight units/min), after which the rate of decrease is lowered 180-fold (1.1 molecular weight units/min).

Spectral measurements indicated destruction of the aromatic conjugated system of methanol-lignin during ozonization. IR and NMR studies on original and ozonized methanol-lignin showed reaction of ozone with aromatic rings, production of carboxyl and aldehyde groups, formation of quinone moieties and low molecular weight substances.

Ozone reacts with the aromatic rings at the highest rates during the early stages, and is accompanied by the most rapid decrease in molecular weight within the first 5 minutes.

Ozone Generator: The apparatus used for ozone production and the gas source were not described.

Contact: The methanol-lignin was ozonized in the solid state on a sintered glass filter 7 cm in diameter, in the stationary phase, at an ozonizing gas flow rate of 600 ml/min, and at 20°C.

References: 24

PU-27

Title: "Soda Lignin III. Lignin-Carbohydrate Bond in Soda Lignin From Hardwoods"

Authors: M.F. Kiryushina & D.V. Tishchenko

Source: Zhur. Priklad. Khim. (Leningrad) 41(8):1848-1853 (1968). Chem. Abstr. 70:12767p (1969)

The acetone-insoluble fraction of maplewood soda lignin (I) (10.7% MeO groups) was subjected to a 2nd soda cook at 170°. The MeO^- group content of the product (II) was increased to 12.85%; however it still contained 34.5% carbohydrates (III). Hydrolysis of I with 1% H_2SO_4 gave a product containing 18.45% MeO^- groups and no III. Also ozonization of soda lignin in EtOAc separated III from I. The infrared spectrum of I had a band at 1740 cm^{-1}, which was absent in acid-hydrolyzed I. This indicates that the lignin/carbohydrate bonds are of the phenylglucoside type.

PU-28

Title: "Bleaching of Pulp With Ozone"

Authors: T. Kobayashi, J. Hosokawa & T. Kubo

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Source: Japan. Kokai 76,139,902, Dec. 2, 1976, Appl. 75/62,660, May 26, 1975. Chem. Abstr. 86:57076 (1977)

Pulp was bleached with ozone at <5° and washed with water alternately to prevent viscosity decrease. Thus, 5 g Douglas fir kraft pulp was sprayed with 45% water, treated with oxygen containing 1% (vol) of ozone at 0° to 5° and 200 ml/min to a whiteness degree of 40%, and washed. The same process was repeated twice to prepare pulp having viscosity of 6.4 cP, compared with 4.9 cP for pulp bleached at 30°.

PU-34

Title: "The Resistance of Hemicelluloses in Wood Fiber to Degradation by Ozone."

Authors: W.E. Moore, M. Effland, B. Sinha, M.P. Burdick & C. Schuerch

Source: TAPPI, 49(5):206-209 (1966).

Review: To investigate the distribution of hemicelluloses within the native plant cell wall, a study was made of the fate of the carbohydrate fraction of wood substance upon extensive gas phase ozonation. The majority of hemicelluloses were easily accessible to ozonation, while some hemicellulose sugars, mannose in particular, were in extremely inacccessible fiber regions. Some preferential attack was observed, with lignin being virtually eliminated by oxidation.

Ozone Generator: A conventional corona discharge laboratory generator using oxygen at a flow rate of 350 ml/min formed ozone at a concentration of 0.8 vol %.

Contactor: Initially, ozonized oxygen was passed through a bubbler containing water, then through a column of wood shavings with 100% water. In some cases never-dried green wood was used, with no significant differences being observed. Pressure was usually about 1.25 atm. Alternatively, a fluctuating pressure was induced by a solenoid valve and water pump, increasing pressure from 230 to 760 mm in about 30 sec. Fresh gas continued to flow for 18 sec. Gases were then maintained on the wood chips for 36 sec, and a vacuum applied for a final 36 sec. Ozonation time was 10 to 30 hrs. Ozonized chips and fibers were disintegrated in water suspension with a high speed metal stirrer. Fibers were filtered and water soluble fractions were obtained by concentrating the liquors and washings. Residual fibers were collected and further ozonized as a loose mat or in suspension with water (0.1% concentration).

Results: Fiber fractions were analyzed for 5 sugars: galactose (I), glucose (II), mannose (III), arabinose (IV), and xylose (V)], lignin (VI) and uronic acid (VII). Values of VII were high because of CO_2 evolution from oxidized carbohydrates. The % of fiber recoverable as identifiable sugars decreased with ozonation time. The average degree of polymerization decreased to 250 to 400, before delignification. Of the sugars, II was the most resistant to

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ozonation, but the % of V was about one-half that present originally. There was a regular decrease in the amount of xylan left in the fiber with increasing ozonation time, but after 20 hrs poplar began to lose II more rapidly than V. In softwoods, the relative proportion of III (the predominant hemicellulose) was reduced by a factor of 2 early in the ozonation, but at higher degrees of ozonation, II was lost more readily.

Fiber isolated after 10 hrs of ozonation was resuspended in water (1 g/100 ml) and re-ozonized for periods up to 3 hrs. Although the degree of polymerization was ca 150, substantial amounts of V and III still were present.

Analyses of the fiber fractions for carbonyl and carboxyl groups were abandoned because of the multiplicity of oxidized functional groups and the impossibility of distinguishing between those functions originally present and those formed during ozonation. A small fraction (5%) of dioxane-soluble material from 30 hrs of ozonation of maplewood, after hydrolysis, appeared to be 2-O-4-O-methyl-α-D-glucopyranosyluronic acid-D-xylose. A small amount of fiber was converted to CO_2 and HCOOH during hydrolysis. Oxidized fragments of original pentoses and hexoses were not identified.

Economics: Cost factors were not presented in this paper.

References: 20

PU-38

Title: "Ozone: A New Method to Remove Color in Secondary Effluents".

Authors: C. Nebel, R. Gottschling & H.J. O'Neill

Source: Pulp & Paper 48(10):142-145 (1974)

Ozone can be effectively used to remove color, reduce levels of COD and turbidity and provide a high degree of disinfection in secondary pulp and paper mill effluents. Since sludge is not generated during ozonization, secondary clarification and dewatering are not required.

PU-39

Title: "Ozone Decolorization of Pulp and Paper Mill Secondary Effluents".

Authors: C. Nebel, R.D. Gottschling & H.J. O'Neill

Source: Proc. 7th Mid-Atlantic Indl. Wastes Conf., Drexel Univ., Philadelphia, Pa. (1974), p. 161-187

Analysis of various decolorization processes for pulp and paper mill effluents indicate that there are 2 processes which deserve strong consider-

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ation: massive lime dosages and oxidation with ozone. Lime is applied prior to secondary treatment whereas ozone is applied after the secondary process. The lime process is relatively expensive to operate. Experimental data show that ozone treatment simultaneously brings about disinfection of the effluent, thus further treatment is not necessary. The costs of color removal from 4 different secondary pulp and paper mill effluents are in the range of 2.8¢ to 6.4¢/1,000 gal. Substantial reductions in [COD], [BOD] and turbidity levels were experienced. Sludge is not developed in the process, therefore low maintenance costs can be expected.

PU-41

Title: "Graft Copolymers of Cellulose; Polymerization Initiated by Decomposition of Cellulose Peroxides"

Authors: L. Neimo, H. Sihtola, O. Harva, & A. Sivola.

Source: Papper och Trä 8:509-516 (1967)

Review: A bleached pine sulfate paper pulp was ozone-treated to graft copolymers of cellulose. Two stages were involved: The 1st was the generation of peroxide groups from the starting material; the 2nd was the decomposition of the peroxides to free macroradicals, which initiated the grafting of polyacrylamide or polyacrylonitrile onto the cellulose backbone. Significant amounts of carbonyl and carboxyl groups were generated along with the peroxides; cellulose molecules were damaged during ozonation, greatly impairing the paper-making properties of the starting material. These properties were improved with the grafting of acrylamide. However, except for special type products (such as ion exchange resins) or if other advantages, such as simultaneous bleaching can be coupled to the process, grafting by ozonation did not appear feasible.

Ozone Generator: A Welsbach T-23 ozonizer. Silica gel-dried oxygen was used in most cases as the source for ozone generation; where [ozone] of <2 vol % was desired, air was used.

Contactor: Small quantities of pulp were ozonized in a vertical glass tube 40 x 500 mm, with a ground glass 2-way stopcock at each end. Gas flow direction was changed every 30 min. On a larger scale, ozonated gas was flushed through the pulp in a round reaction vessel; the flow of gas was interrupted every 10 min to enable mixing of the pulp. Ozonations were conducted for up to 16 hrs at 3.3 vol % of ozone.

Effects of Ozonation: On the average, each 10th anhydroglucose unit in the cellulose chain is oxidized. The rate of formation of aldehyde groups becomes retarded upon longer periods of ozonization, and the development of carboxyl groups is accelerated at the same time. Very rapid depolymerization occurs during the 1st hr, after which a levelling off is observed.

References: 27

PU-44

Title: "The Action of Gaseous Reagents on Cellulosic Materials. II. Pulping of Wood with Ozone."

Authors: Z. Osawa, W.A. Erby, K.V. Sarkanen, E. Carpenter & C. Schuerch

Source: J. Tech. Assoc. Pulp & Paper Industry, 46(2):84-88 (1963b)

Review: The effects of ozone on whole wood and factors influencing the reactions were studied. Rates of attack on holocellulose and lignin were investigated under the following conditions:

1) In a liquid system (water and nitromethane) at 0°C,
2) In a gas-phase system with constant and fluctuating pressures, and
3) On wood of various species, tissues, and particle sizes (mostly small chips of Norway spruce, also veneer strips of gumwood and Douglas fir, shavings of basswood, wheat straw, and small pieces of Douglas fir bark).

Ozone acted as a rather indiscriminant reagent. Results depended greatly on the permeability and rate of transfer of the ozone. Yields of cellulose of 40% to 50% based on wood substance were obtained from certain woods at degrees of polymerization of around 400. Water-soluble products contained methanol and acetic and oxalic acids. 20% of lignin was removed in about 3 hrs in nitromethane, and about 10 hrs in water. After the first few hrs, though, little or nothing was gained in the specificity of attack on lignin by the use of nitromethane. The attack on carbohydrate was slightly slower in nitromethane than in water.

Wood ozonized in air was strongly acid and smelled strongly of acetic acid. With all samples, the reaction in the gas phase was faster and more homogenous than in the liquid phase. Results were further improved by the use of a fluctuating pressure. Reaction in the gas phase was markedly influenced by the moisture content of the wood sample; the optimum moisture content was near 100% in Norway sprucewood samples. The wood species influenced the course of the reaction, with spruces being more difficult to affect extensively than basswood. Plant structure also was an important factor: springwood reacted much more rapidly than summerwood, and Douglas-fir bark was completely impervious to gas transport and did not react at all at atmospheric pressure.

Feedstock: Dry oxygen was used as the source for ozone generation.

Ozone Generator: A conventional laboratory ozonizer was used, consisting of a Pyrex glass mercury well surrounded by a Pyrex glass tubing. The tubing was wrapped in Al foil and exterior insulation, and oxygen was passed through this. A potential of 10,000 v was used.

Contact: 1 g samples of Norway sprucewood meal were suspended in 10 ml of solvent (water or nitromethane) and ozonized oxygen passed through the suspension at 75 ml/min. The substrate was placed in 5 small cells in series; [ozone] was 10.9%. The suspensions of basswood shavings in water and 10% nitromethane (about 10 g) were treated in a glass cylinder with oxygen passing through a sintered glass plate at the bottom of the cylinder and bubbling through the mixture at a flow rate of 283 ml/min and [ozone] of 3.4%. In all other reactions, 2 ozonators were used in series, with a rate of oxygen flow of 1,250 ml/min, [ozone] of 1.0%. The pressure was fluctuated between 1 and 1.4 atm by means of a magnetic solenoid valve opened 4 times/min. The gas stream was passed through water before entering the reactor to prevent drying of the wood chips.

Economics: The economics of the processes were not discussed.

References: 13

PU-45

Title: "Ozonation of Kraft Pulp and Paper Effluents"

Author: R. Ottman (U. of Illinois, Urbana, Ill.)

Source: Private Communication, August 1, 1972 to I. Gellman. Cited in Natl. Council of the Paper Industry for Air and Stream Improvement, Tech. Bull. #269, Jan. 1974, by R. C. Whittemore (p. 2).

"In a study of ozonation of kraft effluents, 50% of the color of a total mill effluent was reduced with 190 mg/l ozone over less than 15 min of contact. Approximately 25% of the COD and less than 1% of the BOD were removed during this period."

PU-46

Title: "Treatment of Industrial Effluents and Gaseous Discharges in U.S. Industries".

Author: A.M. Pristupa

Source: Bumazhn. Promy. (Moscow) 12:23-26 (1974). Air Poll. Tech. Info. Center No. 73936

A survey of pulp and paper mills in the USA concerning water protection and air pollution prevention is presented. In the absence of Federal standards on air pollutant emissions, dust and malodorous gaseous emissions in plants situated in or near communities are limited by local regulations. Soda reclamation plants are equipped with 2 or 3 electrostatic precipitators and additional scrubbers. Venturi scrubbers are used for lime recovery kilns. The use of oxygen and ozone in technical processes in place of other chemicals constitutes a major contribution to air and water pollution abatement.

PU-57

Title: "Coliform Bacteria Growth and Control in Aerated Stabilization Basins"

Author: S.H. Watkins

Source: EPA Report No. 660/2-73-028, 279 pages, Dec., 1973. Pages 220-221 deal with ozonation.

Review: This article was concerned with the effects of chlorination to control coliform bacteria in secondary effluent from a pulp and paper mill plant. A few experiments were made using ozone.

Ozone Generation: Ozone was generated by a Welsbach Model T23 laboratory ozonator operated on tank oxygen. Ozone output was 525 mg/hr.

Ozone Contactor: A sparger was placed in the vertical section of a 3.8 cm (1.5 in) OD rubber hose carrying the waste.

Procedure: Effluent flow through the rubber hose was 5 gpm, and the ozone dosage thus was 0.46 mg/l. Slowing the rate of effluent flow increased the ozone dosage to a maximum of 4.6 mg/l.

Results: No effects on bacterial motility nor upon bacterial concentrations were observed. No residual ozone was found in any of the samples.

Abstractors' Comment: Rubber is one of the most reactive materials with ozone. Thus rubber should not have been used as a contactor. Since no residual ozone was found, and since sulfite mill wastes are known to be high in ozone demand, it is also clear that the ozone dosage was too low. Thus the results of this work are meaningless.

References: 15 (1 dealing with ozone)

PU-58

Title: "Preliminary Laboratory Studies of the Decolorization and Bactericidal Properties of Ozone in Pulp and Paper Mill Effluents."

Authors: R.C. Whittemore & J.J. McKeown

Source: National Council of the Paper Industry for Air & Stream Improvement, Inc., Technical Bulletin #269, January 1974.

Apparatus: An Ozonator Corp. Model 4,000 silent arc discharge generator was used, capable of generating 0 to 30 mg/min of ozone from oxygen.

Contactor: A countercurrent, fritted glass disc, sparged column 90 cm high, 5 cm in diameter, with an approximate volume of 1.8 liters.

Classes of Effluents Studied:

(1) Unbleached kraft effluent synthesized from softwood kraft black liquor diluted to a BOD-5 of 300 mg/l.

(2) Unbleached kraft effluent synthesized from hardwood kraft black liquor diluted to a BOD-5 of 300 mg/l.

(3) Hardwood caustic stage washer bleach plant effluent.

(4) Softwood caustic stage washer bleach plant effluent.

(5) Hardwood chlorine-stage washer plant effluent.

(6) Softwood chlorine-stage washer bleach plant effluent.

(7) Neutral sulfite total mill effluent where recovery is practiced (sodium and ammonia base).

(8) (1 to 6) above after lime decolorization.

(9) Biologically treated boxboard total mill effluent.

(10) Biologically treated sulfite total mill effluent.

Results: For unbleached kraft pulp mill effluent prepared from weak kraft bleach liquors; hardwood bleaching effluents, softwood chlorination stage bleaching effluents and biologically treated bleached kraft total mill effluents, the effluent color decreased with increasing ozone use. However, the amount of color removed was time-dependent, 45 min contact time resulting in better than 80% color reduction, or residual color levels of <100 APHA units. For a given effluent, more color was removed/unit weight of ozone at the shorter contact times of 10 to 20 min.

To achieve 50%, 75% and 90% color reduction required variable amounts of ozone from 1 effluent to another. Up to 10% color reversion (% return of color 24 hrs after ozone treatment had ceased) occurred in many but not all effluents, in the median range of 5% to 8%. This amount of reversion is considered to be significant.

Total coliform counts in kraft total mill effluents showed a rapid decrease with ozone dosages of <100 mg/l, followed by a slow decay to 0 at high ozone dosages of several hundred mg/l. Boxboard mill effluents showed total coliform densities reduced to 0 with [ozone] on the order of 25 mg/l.

Color of ozonized boxboard effluents averaged <200 APHA units, while color of ozonized total mill kraft effluents ranged from 400 to 1,800 APHA units.

Effluent color (as well as SS) appears to be a significant factor in determining the amount of ozone required for disinfection. An increase in color of kraft mill effluent from 400 to 4,000 APHA units and dosing with 300 mg/l of ozone reduced the induced color bacteria and total coliform densities by 15% and 57%, resp. The sample containing fewer color bodies produced 99% kill of total bacteria and 97% kill of total coliforms at lower ozone dosage (190 mg/l).

Splitting a biologically treated kraft mill effluent, then filtering one-half through Whatman No. 42 filter paper, then ozonizing each sample and determining total coliforms showed that lowering levels of SS will result in reduced ozone demand to achieve effluent disinfection (190 mg/l vs. 75 to 120 mg/l to attain 1% or less total coliforms).

In nearly all experiments, [COD] was reduced 0% to 30% upon ozonation, although an occasional 50% reduction was observed. Significant increases in [BOD] were observed, especially for ozonated boxboard and integrated kraft aerated stabilization basin effluents and the Na base NSSC total mill effluent. Some ozonated samples showed 0% to 10% or 0% to 20% reduction in [BOD]. It is postulated that ozonation caused partial oxidation of organic COD components, making them more biodegradable.

However, portions of 3 primary settled kraft total mill effluents were ozonated to remove color, and the remainder of each effluent sample was set aside as controls for biological oxidation studies. Each was seeded, fortified with nutrients and aerated. The data show that ozonation for color reduction up to 50% had no effect upon subsequent biological oxidation. This implies that the nature of the biodegradable material is not affected by ozonation.

In other experiments, data obtained showed that <3 lbs of ozone are required to remove 1 lb of COD (average 1.61). Lime decolorized effluents required an average of 1.72 lbs of ozone/lb of COD.

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LITERATURE CITED (SOAPS & DETERGENTS) (SD)

SD-01* Baer, F.H., 1970, "Ozone Step Allows Recycle of Organic-Fouled Water", Chem. Engrg., Aug., p. 42.

SD-02 Buescher, A., Jr. & D.W. Ryckman, 1961, "Reduction of Foaming of ABS by Ozonation", Proc. 16th Ann. Purdue Indl. Waste Conf., p. 251-261.

SD-03* Evans, F.L., III & D.W. Ryckman, 1963, "Ozonated Treatment of Wastes Containing ABS," Proc. 18th Indl. Waste Conf., Purdue Univ., p. 141-157.

SD-04 Grossman, A., K. Kwiatkowska & M. Zdybiewska, 1970, "Use of Ozone for the Decomposition of Organic Substances in Water." Zese. Nauk, Politech. Slask., Inz. Sanit., (Politech, Slaka, Gliwice, Poland).

SD-05 Kandzas, P.F. & A.A. Mokina, 1969, "Use of Ozone for Removing Synthetic Anionic Surface-Active Agents from Wastewaters". In the book: *Ochistka Proizvodstvennykh Stochnykh Vod.* (Purification of Industrial Sewage), Moscow, 4:76.

SD-06 Kandzas, P.F. & A.A. Mokina, 1968, Trudy Vsesoyuzn. Nauchno-Issled. In-ta Vodosnabzheniya, Knalizatsii Gidrotekhnic heskikh Sooruzheniy i Inzh. Gidrogeologii (Works of the All-Union Scientific Research Institute of Water Supply, Sewage, Hydrotechnical Structures and Hydrogeological Engineering) 20:40.

SD-07 Kuiz, C.G., 1970, Grasas aceit. 21:91.

SD-08 Kwie, W.W., 1969, "Ozone Treats Waste Streams From Polymer Plant", Water & Sewage Works 116:74-78.

SD-09 Mal'kina, I.I. & V.G. Perevalov, 1970, "Removal of Some Nonionic Surface-Active Agents from Water by Ozone Treatment." Neft. Khoz.

SD-10* Marschall, K., 1973, "Process of Treating and Purifying Sewage, Particularly of Sewage Contaminated with Detergents". U.S. Patent 3,733,268, issued May 15.

SD-11* Marschall, K., 1974, "Process of Treating and Purifying Sewage, Particularly of Sewage Contaminated with Detergents". U.S. Patent 3,822,786, issued July 9.

SD-12 Verde, L., Meucci, F. & Vanini, G.C., 1969, Ing. Mod. 62:277.

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SD-01

Title: "Ozone Step Allows Recycle of Organic-Fouled Water."

Author: F.H. Baer

Source: Chem. Engrg., August, 1970, p. 42

Ozonation of carwash waste, including detergents, in Vienna, Austria, is discussed. The treatment process includes oil separation and skimming, sedimentation (3 hrs with or without flocculation agents), gravel filter (removes fine sediment) and ozonation (15 to 20 min reaction with recirculation). Total system capacity is 19,915 gal/day. With this treatment system for recycle, only 793 gal/day of fresh water needs to be added.

Ozone System: Not specific. A 4-column generator producing 4 g of ozone/hr (12 to 15 kv electric field)

Cost: $23,000 for treatment process. This compares with a fresh water well source costing $61,000, with no means of wastewater disposal provided.

SD-03

Title: "Ozonated Treatment of Wastes Containing ABS"

Authors: F.L. Evans, III & D.W. Ryckman

Source: Proc. 18th Indl. Waste Conference, Purdue Univ. (1963), p. 141-157

Review: ABS (alkyl benzene sulfonate) detergents are made more amenable to biodegradation as a result of partial chemical oxidation by ozone.

Experimental: Sewage was employed from a treatment plant employing biological primary and secondary treatment and which contained ABS. Sample sizes taken were 45 gal. [ABS] was 6.4 mg/l in the actual sewage and an amount of ABS surfactant equivalent to 10 mg/l was added to a portion of the plant effluent. A 3rd sample of 50 mg/l ABS in distilled water was prepared. All 3 samples were ozonized and their biochemical behaviors were determined under simulated stream conditions by observing the progression of BOD.

Ozonation System: A Welsbach T-23 generator operating on air which had been passed through a glass wool/cotton grease and dirt trap, then activated alumina to a -60°F dew point.

Contactor: A single 10 ft column consisting of 5 3-inch ID diameter Pyrex glass sections, with a vertical mixing recirculating system in the lower section, and sampling ports at various heights.

A 3.8 liter sample was placed in the column then ozonized for periods of time ranging from 2 to 120 min. At the end of each run the volume of gas

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passed through the wet test meter was recorded, the amount of unreacted ozone determined by titration and the ozonized liquids analyzed for ABS, COD and BOD. Secondary effluent samples and those with 10 mg/l added ABS were ozonized in duplicate for 2, 5, 10, 20, 30, 45, 60, 90, and 120 min. The 50 mg/l ABS in distilled water sample was ozonized at an ozone/air flow rate of 0.1 cfm for periods of time up to 120 min. BOD only was measured on these samples after ozonation.

Results: Removal of ABS from fortified (with ABS) and unfortified samples was rapid at first, then began to taper off at 45 mg/l and 25 mg/l, resp, of absorbed ozone. Reduction of [ABS] from 6.4 to 1.0 mg/l (unfortified sample) required 150 mg of ozone; reduction from 16.4 to 1.0 mg/l (fortified sample) required 250 mg of ozone. Thus, the additional 10 mg/l of ABS required 100 mg of ozone; or 2.64 mg/l of ozone was required to remove 1 mg/l of ABS from the samples.

The greater the starting [ABS], the greater the amount that could be removed while maintaining the ozone transfer efficiency at a high enough level (86% to 90%) for process practicality. As the quantity of ozone used increased, the COD of all samples decreased.

BOD-5 of effluent samples was reduced to 0 by absorption of 180 mg/l ozone, but twice as much ozone was required to reduce [BOD] of the fortified sample to 1 mg/l. [BOD] of the fortified sample increased up to that point of ozone absorption at which the [ABS] was no longer detectable. Thus at low [ozone], ABS is converted to intermediates which are biodegradable. At higher [ozone], the ozonized products are further oxidized such that they no longer exert a BOD. While ozone lowered the COD of ABS, it increased the amount of material which could be utilized by the microorganisms.

The 50 mg/l ABS in distilled water sample showed an inhibitory effect on activated sludge organisms. After 10 min of ozonation, inhibitory action no longer was evident and ozonized ABS served as the sole food source. By increasing the amount of applied ozone, the rate of biological reaction increased. After 4 hrs in the Warburg respirometer, oxygen utilization in the sample ozonized 15 min was 29 mg/l, but was 55 mg/l in the sample ozonized 120 min, an increase of 370%.

The authors postulate that when alkylbenzenes are ozonized, the alkyl group is converted to a carboxyl group, the point of initial attack being the carbon atom attached to the benzene ring. Upon continued ozonation, the aromatic ring is ruptured.

Conclusions: 95% removal of 5.9 mg/l ABS required 100 mg/l of ozone (at 83% utilization efficiency) and 95% removal of 15.6 mg/l ABS in the fortified sample required 75 mg/l of ozone dosage (at 92% ozone transfer efficiency). Ozonation reduced levels of both COD and BOD. Increasing dosages from 53 mg/l of ozone (sufficient to eliminate foaming) to 100 mg/l of ozone produced a significant increase in [BOD]. Ozonation of 50 mg/l of ABS in distilled water destroyed its biological inertness. Ozonized ABS solution

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served as the oxidizable substitute for microbes, and an increase in ozone dosage increased both the amount of material available for biological oxidation and the biochemical oxidation rate.

References: 27

SD-10

Title: "Process of Treating and Purifying Sewage, Particularly of Sewage Contaminated with Detergents"

Author: K. Marschall

Source: U.S. Patent 3,733,268, issued May 15, 1973, Filed Dec. 8, 1970

Car washing wastewater is passed through an oil separator for removal of oil, grease, fat, solvents, etc. Air is bubbled through this container to accelerate separation of oil and to strip volatile solvents. In a 2nd container flocculating agents are metered in, the settled liquid passed through a gravel filter to remove fine particles, then to countercurrent ozonation in a steel or concrete contactor. An activated carbon filter can be used to break down excess ozone in the exhaust gases, which then may be used in air conditioning systems. The ozonized water also is passed through an activated carbon filter prior to recycle and reuse.

Makeup water is supplied to the top of the gas-liquid contactor. Water in the contact chamber is also recycled from the bottom to the top, by means of a pump to increase efficiency of ozone contacting.

SD-11

Title: "Process of Treating and Purifying Sewage, Particularly of Sewage Contaminated with Detergents"

Author: K. Marschall

Source: U.S. Patent 3,822,786, July 9, 1974; filed June 30, 1972

A division of U. S. Patent 3,733, 268, by the same inventor; identical with 3,733,268, except that more patent claims are made.

TYPING GUIDE SHEET

LITERATURE CITED (TEXTILES) (TX)

TX-01 Anonymous, 1973, "Japanese Develop Water Treatment", Daily News Record 3(9):23.

TX-02* Anonymous, 1974a, "Ozone-Carbon Dye-Waste Treatment", Textile Ind. 138(10):43, 45.

TX-03 Anonymous, 1974b, Gijutsu to Kogai 4(4):22-28.

TX-04* Anonymous, 1975a, Kogai 10(4):20-27.

TX-05* Anonymous, 1975b, Kogai 10(4):34-48.

TX-06* Anonymous, 1975c, Kako Gijutsu 10(8):31-36.

TX-07* Anonymous, 1976a, Netherlands Patent NL 7506-370 (Dec 2, 1975). Derwent Netherlands Patents Report W(51):D2, Jan 27.

TX-08* Anonymous, 1976b, Mizushori Gijutsu 17(1):53-62.

TX-09* Anonymous, 1976c, Textile World 126(11):108, 111, 113, 115, 116, 118, 121.

TX-10 Bauch, H. & H. Burchard, 1970, "Experiments to Improve Highly Odorous or Harmful Sewage with Ozone", Wasser, Luft u. Betrieb 14(4):134-137.

TX-11 Best, G.A., 1974, "Water Pollution and Control", J. Soc. Dyers & Colourists (Great Britain) 90:389-393.

TX-12 Horikawa, K., H. Wako & E. Sato, 1976, "Treatment of Dye Waste Effluents by Ozonation with Ultraviolet Radiation", Kogyo Yosui 214:21-24.

TX-13 Ikehata, A., 1975, "Dye Works Wastewater Decolorization Treatment Using Ozone", in Ozone for Water & Wastewater Treatment, R.G. Rice & M.E. Browning, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 688-711.

TX-14 Kawazaki et al., 1965, Water & Wastewater (Japan) 6:643-648, 778-780.

TX-15 Maeda, M., Y. Hashimoto, T. Ozawa, T. Imamura, M. Matsuoka & N. Tabata, 1972, "Ozone Treatment of Dyeing Wastewater", Mitsubishi Denki Giho, 46(10):1110-1115.

TX-16* Maeda, S., 1974, "Studies on the Liquid Waste Treatment of Dye Manufacturing Plants (II)", Gijutso to Kogai (Technology & Public Nuisance) 4(4):22-28.

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TX-17 Maggiolo, A., F. Davis, N. Lowe & R. Montgomery, 1977, "Ozone vs Chlorine in Treatment of Textile Chemical Wastes; Its Problems and Possible Solutions", presented at 3rd Intl. Symp. on Ozone Technology, Paris, France, May. Intl. Ozone Assoc., Cleveland, Ohio.

TX-18* Matsuoka, H., 1973, "Ozone Treatment of Industrial Wastewater", PPM 4(10):57-69.

TX-19 Mizumoto, K. & M. Horie, 1974, "Dyeing Wastewater Treatment by Combination of Ozone and Activated Carbon", Japan Textile News 89:238.

TX-20* Nakayama, S. & M. Maeda, 1976, "Decoloring Mechanism of Dyes with Ozone and the Effect of pH", Mizu Shori Gijutsu 17(2)157-161. Chem. Abstr. 86:60133f.

TX-21 Nebel, C. & L.M. Stuber, 1976, "Ozone Decolorization of Secondary Dye Laden Effluents" in Proc. Second Intl. Symp. on Ozone Technology, R.G. Rice, P. Pichet & M.-A. Vincent, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 336-358.

TX-22* Netzer, A., 1976, "Advanced Physical-Chemical Treatment of Dye Wastes", Progress in Water Technology 8(2-3):25-37.

TX-23 Netzer, A., S. Beszedits, P. Wilkinson & H.K. Miyamoto, 1976, "Treatment of Dye Wastes by Ozonation", in Proc. Second Intl. Symposium on Ozone Technology, R.G. Rice, P. Pichet & M.-A. Vincent, Eds., Intl. Ozone Assoc., Cleveland, Ohio, p. 359-373.

TX-24* Rinker, T.L., 1975, "Treatment of Textile Wastewater by Activated Sludge and Alum Coagulation". Blue Ridge-Winkler Textiles, Bangor, PA., NTIS Report PB-248,142/2 WP. EPA Rept. No. EPA/600/2-75-055, Oct., 216 pages.

TX-25* Sato, S., K. Yokoyama & T. Imamura, 1974, "Decomposition of Azo Dyes by Ozone." Preprint, 31st fall Mtg., Chem. Soc. of Japan, Oct. p. 614.

TX-26 Smirnova, L.V. et al., 1972, "Use of Ozone for Purification of Effluent from Nitron Fibre Production", Khim. Volokna, (USSR) 14(1):70. World Textile Abs., 4:4016 (1972).

TX-27* Snider, E.H. & J.J. Porter, 1974, "Ozone Treatment of Dye Wastes", J. Water Poll. Control Fed. 46(5):886-894.

TX-28* Stuber, L.M., 1973, "Tertiary Treatment of Carpet Dye Wastewater Using Ozone Gas and Its Comparison to Activated Carbon", Special Rsch. Prob., School of Civil Engrg., Georgia Inst. Tech., Atlanta, GA, Aug., 17 pp.

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TX-29 Stuber, L.M., 1974, "Tertiary Treatment and Disinfection of Tufted Carpet Dye Wastewater." Engrg. Bull., Purdue Univ. Ext. Ser., 145(2):964-977.

TX-30 & 31 & 32 Stuber, L.M., 1975a,b,c, "Tufted Carpet Dye Wastewater Treatment, Pt. I." Indl. Wastes, Jan/Feb 1975(a); "Pt. II", Mar/Apr 1975(b) 29-30; "Pt. III", May/June 1975(c) 13-14.

TX-33* Tsukabayashi, K., 1975, "Treatment of Wastewater from Textile Dyeing Processes", Yuki Gosei Kagaku Kyokai-shi 33(5):377-383.

TX-34 Urushigawa, Y., G. Kurata & Y. Noji, 1974, "Treatment of Dyeing Wastes by Trickling Filter and Ozone Treatment System", Kogai (Poll. Contr.) 9(3):118-124.

TX-35 Yamashita, Y., H. Asai & K. Kitano, year unknown, "Treatment of Dyeing and Finishing Effluent with Ozone" Sen'i Kako 25(5):289-302.

TX-36 Tsukabayashi, K., 1975, "Treatment of Wastewater from Textile Dyeing Processes", Yuki Gosei Kagaku Kyokai-shi 33(5)377-383.

TX-02

Title: "Ozone-Carbon Dye Waste Treatment"

Author: Anonymous

Source: Textile Ind. 138(10):43,45 (1974a)

Review: Recently, waste dyeing water has been recognized as a part of environmental pollution and research has commenced on several new treatment techniques. One new technique is based on a combination of ozone and GAC. Oxidation by ozone and adsorption by GAC to treat wastewater is well documented. Less well known is the synergistic effect of these methods when combined. The combined use of ozone and GAC, as compared with the separate use of each, often will produce a doubled effect and result in low investment costs.

The ozone/GAC process is free of the disadvantages of sludge production that occur with conventional processes such as coagulative/precipitation or activated sludge. The process basically involves decomposing and decoloring dyes in the wastewater by ozone, while decomposing dissolved organic substances and then removing dirt by GAC. The GAC is removed periodically after use and regenerated at high temperatures.

The process has the following advantages: effective decoloration and removal of organic substances in addition to increased treatment power of the GAC; extremely high decoloration power of ozone; no foaming of treated water because of surface active agents being decomposed; removal of noxious substances such as phenol; no sludge production; no particular location requirement for the installation; only a small area needed for the installation because of its compact size; simplicity in automatic operation and ease of maintenance; high performance and stability of the ozone generators; high adsorption power and regeneration efficiency; a synergistic effect from their combinatio; low operating costs; and no secondary pollution.

The Japanese plant described currently is treating 870,000 gpd at a cost of about $0.34/1,000 gal, with few of the problems associated with conventional processes. Ozone is produced easily, by silent discharge; the GAC is regenerated at intervals for reuse. A process flow diagram, specifications of the installation, and examples of the treatment and results are given.

TX-04

Title: Unknown

Author: Anonymous

Source: Kogai 10(4):20-27 (1975a)

Review: Oil/water emulsions frequently are used in the oiling process of fiber dyeing. These emulsions produce high values of COD, BOD and n-hexane extractibles in the wastewater which, in turn, increase turbidities. Various types of dyeing wastewater were treated by ozone with an inorganic coagulant and the removal of the emulsions determined. The process could remove ca 100% of the oil emulsion and colored organic compounds. The sludge formed was 33% to 50% of the normal volume.

TX-05

Title: Unknown

Author: Anonymous

Source: Kogai 10(4):38-48 (1975b)

Studies were conducted on the treatment of wastewater from the towel dyeing industry in Japan. To comply with the 1971 pollution regulations of Japan, it was necessary to install an overall storage tank for wastewater from various sources. During a detention time of about 0.5 day, the pH was maintained in the range 6.5 to 8.0 by an automatic pH regulator. It was also necessary to install an aeration basin capable of aerating the wastewater for about 4 hrs in order to mix the wastewater with air and increase the [DO].

Coagulation/sedimentation was investigated as a method for lowering [COD]. Addition of 100 to 600 mg/l of Al sulfate, a high polymer coagulant, and 2 ml/l of an emulsion of $Ca(OH)_2$ achieved removals of [COD] of nearly 50%. However, the method is not recommended because of the large amount of sludge produced. Trickling filter and activated sludge were effective methods for reducing [COD] to <100 mg/l.

Ozonation was effective for treating wastewaters from factories using reactive dye, but was ineffective for those containing threne, naphthol and/or sulfur dyes. However, since about 90% of the dye used in the towel dyeing industry in the Ehime Prefecture is reactive dye, treatment with ozone is a viable method for this area. Treatment with GAC also was effective in the decolorization, which effect was greatly enhanced by the combined use of GAC with ozone.

TX-06

Title: Unknown

Author: Anonymous

Source: Kako Gijutsu, 10(8):31-36 (1975c)

The general applications of ozone treatment for wastewaters containing dyes include decolorization, decomposition of surfactants, and reduction of [COD] and [BOD]. The amount of ozone required for decolorization is higher for effluents containing disperse dyes than for wastes containing hydrophilic dyes. The weight ratio of added ozone/dye ranges from 0.5 to 1.0 for wastes containing hydrophilic dyes, but is >1 for wastes containing disperse dyes. Disperse dyes which have a high solubility can be decolorized with a smaller amount of ozone because of the higher contacting efficiency of dyes with ozone during treatment.

If a pretreatment method, such as coagulation-precipitation is used prior to ozone treatment, most of the disperse dyes will be removed from the wastewater. However, the removal of hydrophilic dyes cannot be accomplished by coagulation-precipitation. The strong oxidizing ability of ozone permits the oxidation and decomposition of chromophoric groups in dyes, leading to the decolorization of wastewaters containing such dyes.

The presence of reducing substances, such as dithionites, in wastewater interferes with the decolorization of dyes because these substances will consume the ozone present before dyes can react with the ozone. Therefore, separation of these substances prior to ozone treatment is desired.

TX-07

Title: Unknown

Author: Anonymous

Source: Netherlands Patent NL 7506-370 (Dec 2, 1975). Derwent Netherlands Patents Report, W(51):D2, Jan 27, 1976(a)

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Describes a method for treating dye-works effluents so that they are suitable for recycling. Neutral wastewater containing organic dyes and auxiliary agents is subjected to continuous oxidative degradation with ozone in several stages with strong agitation. The amount of ozone applied is adjusted according to the duration of treatment and the oxidation parameters in each stage. This process provides for continuous operation with optimum use of ozone. No supplemental purification steps are required for complete degradation of the dyes and a wide range of dyes/auxiliaries can be degraded. Economic efficiency is assured due to the optimal use of ozone.

TX-08

Title: Unknown

Author: Anonymous

Source: Mizushori Gijutsu, 17(1):53-62 (1976b)

Wastewater treatment by immobilized activated sludge was studied and its application for dyeing factory wastewater was tested. Fixation of activated sludge on polyurethane sponge, polypropylene synthetic cotton, polyethylene sponge and polyethylene thread was examined. All of the substrates could retain >3,000 mg of sludge/l. Polypropylene synthetic cotton retained the highest [sludge], ca 13,000 mg of sludge/l.

Wastewater from a dyeing factory was treated with activated sludge fixed on polyurethane sponge. More than 24 hrs of aeration was required to remove 90% of the 300 mg/l [BOD] in the raw water; however, 3 hrs of aeration was sufficient to obtain a 100 mg/l level of BOD in the treated water. COD removal efficiency was 40% and 70% after 1.5 and 48 hrs of aeration, resp.

The treated water had a pH of 7 to 8, compared to a raw water pH of 10. The color intensity measured at 280 nm decreased to 10% to 60% of the color intensity of the raw water; intensity at 500 nm decreased to 10% to 80% of that of the original.

Decolorization efficiency increased with increased aeration time, but not significantly. Although this treatment was sufficient to lower the [BOD] to acceptable levels, it was necessary to inject ozone into the aeration bath in order to achieve acceptable [COD] values.

TX-09

Title: Unknown

Author: Anonymous

Source: Textile World, 126(11):108, 111, 113, 115, 116, 118, 121, Nov., 1976c

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Several aspects of pollution and energy savings in the textile industry were discussed. The problem of substances used in permanent press processing of cotton which could produce carcinogens was investigated. A major concern was the correction of water pollution caused by effluents from textile works.

Tests were conducted on dye bath, scour and rinse waters from the dyeing process. In several cases, high levels of BOD, TOC, or ammonia-N were explained by known additions to the dye bath. [BOD] was reduced by biological treatment, but [TOC] reduction was not as great, suggesting the presence of materials which were not readily biodegradable. Biological treatment was not successful in color removal, but a treatment which combined alum and powdered activated carbon was quite effective. Lime was an effective treatment for wastewater containing $CaCO_3$ forming levels of carbonate alkalinity.

Reactive and basic dye colored water was successfully treated with ozone, but it could not adequately decolorize wastewater colored by disperse dyes. 1,2,4-Trichlorobenzene, a dye carrier, is biodegradable and 65% or more of it can be removed in a well aerated basin.

For small plants a fixed bed adsorber system with no on-site regeneration system was suggested. Larger plants were urged to incorporate a pulsed bed system with an on-site regeneration system for recycling spent carbon. Combined activated carbon and biological treatment systems are being tested.

TX-16

Title: "Studies on the Liquid Waste Treatment of Dye Manufacturing Plants. (II)"

Author: S. Maeda

Source: Gijutsu to Kogai (Technology & Public Nuisance), 4(4):22-28 (1974)

Waste constituents to be treated include soluble organics (I) (p-aminophenol, p-nitrophenol, their isomers and various intermediate products), Na sulfide (II) and Na thiosulfate (III). [COD] values normally are 40,000 to 60,000 mg/l. I can be removed by polymerization with HCHO, which also reduces [II] and [III] by about 10%, and results in about 50% reduction in [COD] if applied as the 1st treatment step. II then can be removed by reduction of pH to 3.0 to 3.5 and oxidation with air, SO_2 or chlorine (no pH adjustment using chlorine) or by $FeSO_4$. III then can be removed by ozone oxidation or acidic decomposition, producing 83% to 85% overall reduction in [COD] (to 6,000 to 10,000 mg/l). Subsequent neutralization and alkaline ozone oxidation produces a final [COD] of 3,000 to 4,000 mg/l (92% to 94% total removal).

Na thiosulfate pentahydrate (60 g) in 6 l of water containing 20 g of NaOH was completely decomposed in 7 hrs with 25.87 g of ozone (1.47 g of III

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oxidized/g of ozone). In the acidic ozonation of III, only a small amount of ozone is required. Thus 125 g, 250 g and 750 g of III in 100 ml of 1:1 H_2SO_4 required 3.49 g, 5.29 g and 6.73 g, resp., of ozone for total destruction. Without ozone, acidic decomposition of III was somewhat >80%.

Ozonation of 1 liter of alkaline dye waste liquid ([COD] 40,000 mg/l) 11.5 hrs with 42.5 g of ozone gave 30% reduction of [COD].

Formalin (10 ml) treatment of 1 liter of alkaline dye waste liquid, followed by condensation and removal of I ([COD] now 45,000 mg/l) and 8 hrs treatment with 29.6 g of ozone, gave 90.3% removal of COD.

A 4 l sample of alkaline dye wastewater was treated with formalin to remove I, $FeSO_4$ to remove II and acidic decomposition to remove III, then (2,650 mg/l COD) was treated by alkaline ozonation. In 2 hrs the [COD] was reduced 57.8%, and in 7 hrs, 87.2% (to 981 mg/l).

Ozone Generator: Mitsubishi-Denki Model OS4, adjusted to produce 3.74 g/hr from air at a flow rate of 3.74 l/min. KI was used to follow the amount of ozone generated.

Contactor: 2 rigid PVC tanks were used, 1 19-cm in diameter X 70 cm high, the 2nd 13.5 cm in diameter X 49 cm high. Both used porous dispersion tubes at the base of the tanks.

Economics: Not mentioned

TX-18

Title: "Ozone Treatment of Industrial Wastewater"

Author: H. Matsuoka

Source: PPM 4(10):57-69 (1973)

Reviews the generation, properties and contacting of ozone, and its use in treating drinking water and industrial wastewaters.

Cyanides are converted to cyanate (ozone/CN^- ratio = 3) then to carbonate (ozone/CNO^- ratio = 2). Phenols can be removed from solution at an ozone/-phenol ratio of 2.

Studies by Kawazaki *et al*. are cited (TX-14) in which surface active agents were more than 90% decomposed with a 5-fold excess of ozone. Kawazaki also used activated carbon to adsorb surface active agents, then regenerated the activated carbon with ozone (details not given). Studies by the present author show that surface active agents are attacked only after dyestuffs are decomposed and decolorized by ozone.

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Ammonium ion is oxidized quickly with ozone at pH 7.5 to 8.0 (Abstractors' Note: Singer & Zilli [IC-10] found oxidation of ammonia occurs only above pH 9). Zeolite acts as an effective catalyst for this reaction. Sulfite and nitrite are easily ozonized, and organic mercury compounds can be converted to "inorganic substances."

7 Japanese dye manufacturing plants are using ozone for treating wastewaters, as follows (date installed):

Mitsubishi-Denki: Press and float, ozonation [12,000 cu m/day, 16 kg/hr ozone (Aug. 1973)].

Mitsubishi-Kurogawa Industries: Coagulation, ozonation [100 cu m/hr, 2.4 kg/hr ozone (Oct. 1971)].

Kyoshenski-Mitsubishi: Filter, activated carbon, ozonation [50 cu m/hr, 1.2 kg/hr ozone (April 1973)].

Organo-Shobo (Ozone Fuji-Denki): ozonation, activated carbon [3,300 cu m/day, 7.2 kg/hr ozone (summer 1973)].

Nishimo-Mitsubishi: Press and float, ozonation, activated sludge [200 cu m/day, 1 kg/hr ozone (Jan. 1973)].

Ozonation using pretreatment with spray filter beds has been developed by Fukui-Senkyoshi.

For water recycling, Mitsubishi-Juko (Ozone Mitsubishi-Denki) uses secondary treatment, coagulation, sand filtration, ozonation and activated carbon (1,800 cu m/day, 300 g/hr of ozone).

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TX-20

Title: "Decoloring Mechanism of Dyes with Ozone and the Effect of pH"

Authors: S. Nakayama & M. Maeda

Source: Mizu Shori Gijutsu (1976) 17(2):157-161; Chem. Abstr. 86:60133f

Aqueous solutions of Alizarin S (I) and Naphthol Yellow (II) were reacted with ozone at 25°. Initial [I] of 50, 100 and 200 mg/l were used to determine the reaction order with respect to ozone. A first order reaction was observed for the dye and ozone, individually. The decolorization rate of I increased with increasing pH, but more ozone was required with increasing pH, i.e., the efficiency of decolorization declined. For II, pH did not appear to affect the rate, but the efficiency decreased with increasing pH. The mechanism of decolorization of dyes with ozone is discussed in relation to these results and quantum chemistry.

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TX-22

Title: "Advanced Physical-Chemical Treatment of Dye Wastes"

Author: A. Netzer

Source: Progress in Water Technology 8(2-3):25-37 (1976)

A research program was undertaken to characterize the effluents from the dyehouses of various textile mills and to examine the success of color, soluble organic and heavy metals removal from these wastes by massive lime coagulation, activated carbon adsorption, ozonation, and polymeric adsorption. In the lime dosage studies, 0.1, 0.3, 0.5, or 1.0 g of $Ca(OH)_2$ was added to 200 ml of dyebath effluent samples, the mixtures stirred rapidly 3 min, and allowed to settle 1 hr. The supernatants were decanted, filtered, adjusted to a pH of 7.6, refiltered and analyzed for color, TOC, and heavy metals. Various amounts of activated carbon were added to 200 ml dyebath effluent which then was stirred rapidly for 0.5 hr, filtered, and analyzed.

Compressed dry oxygen was fed to an ozonator at a rate to yield an oxygen-ozone flow rate of 1 l/min containing 25 mg/l of ozone. The oxygen-ozone mixture was sparged into a 250 ml gas-washing bottle containing 100 ml of dyebath effluent. After 20 min, the ozonation was stopped, and the sample was filtered and analyzed. Five ml of hydrated resin was added to 150 mg/l solutions of various dyes, the mixtures shaken 24 hr at 300 RPM, the supernatants decanted and filtered, and the concentrations of dye remaining in solution were determined by measuring the transmittance of the samples and comparing the values with those on specially prepared calibration curves.

Lime coagulation gave excellent removals of free heavy metals and in some cases very good color removals as well. Substantial reductions in [soluble organics] and [color] were obtained by activated carbon and resin adsorption. Ozonation was very potent for decreasing color intensity but not for reducing [soluble organics].

TX-24

Title: "Treatment of Textile Wastewater by Activated Sludge and Alum Coagulation"

Author: T.L. Rinker

Source: Blue Ridge-Winkler Textiles, Bangor, PA. NTIS Report PB-248,142/2 WP. EPA Rept. No. EPA/600/2-75-055, Oct. 1975, 216 pages

Reports treatment of wastewater from a textile mill producing synthetic knit fabric for the apparel and automotive markets, with a system combining biological (activated sludge) and chemical (alum coagulation) processes. Treatment consisted of: heat recovery; equalization; completely mixed

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activated sludge with sedimentation and nutrient supplement; and alum coagulation with sedimentation, polymer addition, and pH adjustment.

Activated sludge effectively removed degradable organics and ammonia-N. Alum coagulation effectively removed colloidal organics, SS, orthophosphate, and certain metals. Total treatment system removals for BOD, COD and color were 92%, 73%, and 69%, resp. The capital cost of the system was $1.15 MM with a yearly operating cost of $269,030, including capital depreciation.

Additional treatment was required to meet anticipated discharge limitations. Research studies were conducted using carbon adsorption, resin adsorption, and ozonation for residual, soluble color removal.

TX-25

Title: "Decomposition of Azo Dyes by Ozone."

Authors: S. Sato, K. Yokoyama & T. Imamura

Source: Preprint, 31st Fall Mtg., Chem. Soc. Japan, Oct. 2-5, 1974, p. 614

Scope: Determination of color removal from wastewaters containing azo dyes with a secondary study of the degradation products after ozonation.

Method: Water soluble and insoluble dyes were tested. Methyl Orange was used as a soluble dye and a 100 ml solution was ozonized in a 300 ml bottle. With water insoluble dyes, 20 ml CCl_4 + 10 ml water was used. Ozone was fed at a rate of 24 mg/l/min and its consumption was measured by KI.

Results: Major products of ozonation were identified by gas chromatography, infrared spectrometry, mass spectrometry and various chemical methods and results were as follows: from azobenzene: azoxybenzene, oxalic acid (I) and glyoxylic acid (II); from p-aminoazobenzene and p-dimethylaminoazobenzene: nitrosoazobenzene, nitroazobenzene, I, II and nitrate; from p-hydroxyazobenzene: I and II; from p-methoxyazobenzene: I, II and nitrate; from Methyl Orange: I, II, nitrate and Na bisulfate. Minor oxidation products also were detected by gas chromatography. p-Aminoazobenzene was 100% destroyed by ozonation for 8 min.

TX-27

Title: "Ozone Treatment of Dye Wastes"

Authors: E.H. Snider & J.J. Porter

Source: J. Water Poll. Control Fed. 46(5):886-94 (1974)

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Ozone was used in a series of experiments to determine its ability to degrade textile dye wastes. Dye wastes were analyzed for COD, color, total solids, volatile solids and dissolved solids before and after they were treated with ozone at 3 pH levels. Ozone reduced the color of the dye wastes, but measurements were affected by high turbidity.

TX-28

Title: "Tertiary Treatment and Disinfection of Tufted Carpet Dye Wastewater"

Author: L.M. Stuber

Source: Special Research Problem, School Of Civil Engrg., Ga. Inst. of Technology, Atlanta, Ga. (Aug. 1973), 17 pp.

Review: Describes a study of ozonation as a tertiary treatment of carpet dye wastewater following secondary biological processing.

Contacting: A 5.5 inch x 8 ft cylindrical Plexiglas column with ozone supplied via a 60 μ, high density polyethylene diffuser. Extra dry oxygen was supplied to the ozone generator under pressure. Contact times were not noted. Ozone was determined in the influent and effluent gases.

Results: After various doses of ozone were applied (graphical display for each parameter tested) the following were observed:

1. COD levels: dramatically decreased up to 40% to 45% with 45 mg/l of ozone, then levelled off. SS did not significantly enhance reduction of [COD].
2. Fecal Coliforms: not present at ozone dosages above 25 mg/l.
3. Total Coliforms: <100/100 ml at 45 mg/l of ozone.
4. True color: reduced to <30 APHA units at 40 mg/l of ozone. Reduction in [SS] lowered the necessary ozone dosage to 26.5 mg/l.
5. [Soluble organic carbon] increased slightly with increasing ozone dosages when SS were present, but eventually decreased at extremely high dosages.
6. [SS] lowered 90%.
7. [BOD] increased 150% at 8 to 15 mg/l of ozone, but was unchanged at dosages >25 mg/l.
8. [Biphenyl] was reduced to 0.1 mg/l from 2 mg/l with 89 mg/l of ozone.

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9. [Anionic detergent] was reduced to 0.1 mg/l from 0.6 mg/l with ozone dosages of 15 mg/l.

10. Foaming problems were reduced and eliminated with ozone dosages of 50 to 100 mg/l.

11. DO residuals: 40 mg/l when oxygen was used for ozone generation.

12. Ozone residuals dissipated totally after 20 min.

13. Transfer efficiency of ozone was 85% to 100% with dosages of up to 50 mg/l of ozone.

References 20

TX-33

Title: "Treatment of Wastewater From Textile Dyeing Process"

Author: K. Tsukabayashi

Source: Yuki Gosei Kagaku Kyokai-shi 33(5):377-383 (1975)

Treatment methods for wastewater discharged from textile dyeing processes are reviewed. These are coagulation-precipitation, flotation, filtration, adsorption and biological methods. The coagulation-precipitation method removes about 60% of the BOD and COD from the wastewater and 90% of the color. However, the large quantity of sludge generated is one of the problems with this method. The flotation method has a larger surface loading capacity for wastewater treatment than coagulation-precipitation, permitting use of a smaller facility with the flotation method to achieve the same results as a larger coagulation-precipitation facility. Both these methods are very effective in the decolorization of wastewater.

Selection of the appropriate coagulation agent will permit removal of most dyes. The adsorption method by activated carbon or bauxite is suitable as a secondary treatment method for wastewater rather than as a primary method. The presence of Cr, Cu, Cl and aldehydes in wastewater can be toxic to biological activity.

Ozone treatment is excellent but very expensive; it can be used as a secondary treatment method. Any combination of these methods will produce water which will meet water quality standards. A completely closed system of water/wastewater is difficult to maintain in textile plants because of the high quality of water that is needed in some of the individual processes.